

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number
WO 03/000557 A2(51) International Patent Classification⁷: B65D

(21) International Application Number: PCT/US02/20161

(22) International Filing Date: 24 June 2002 (24.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/888,805 25 June 2001 (25.06.2001) US(71) Applicant (for all designated States except US): PHO-
TONIC BIOSYSTEMS, INC. [US/US]; 21806 NE First,
Sammamish, WA 98074 (US).

(72) Inventors; and

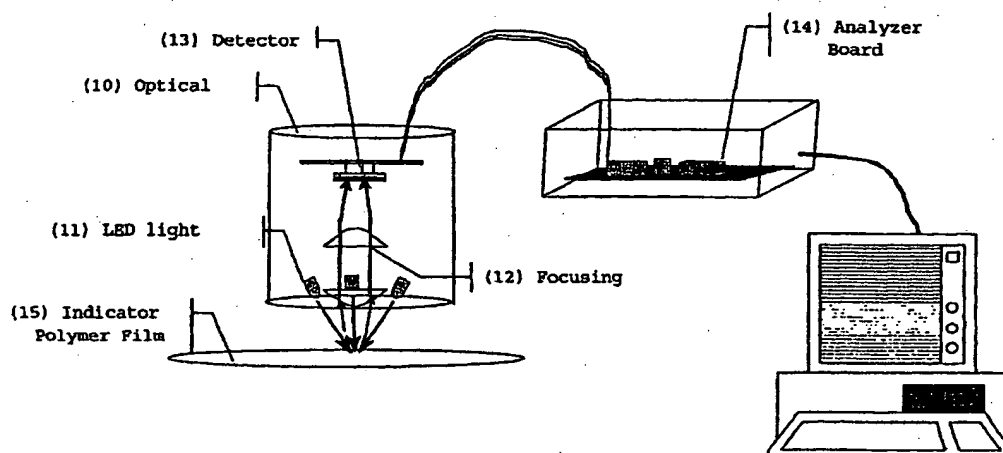
(75) Inventors/Applicants (for US only): PUTNAM, David
[US/US]; 21806 NE First, Sammamish, WA 98074 (US).
HUBBARD, Todd [US/US]; 20221 41st Place NE, Lake
Forest Park, WA 98155 (US).(74) Agent: CONFORTI, Vita, G; Davis Wright Tremaine,
LLP, 2600 Century Square, 1501 Fourth Avenue, Seattle,
WA 98101-1688 (US).(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that reportFor two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR FORMING POLYMER STRUCTURES CONTAINING AN OXYGEN SENSOR

Optical instrumentation used for lifetime measurements



(57) Abstract: There is disclosed a process for melting a luminescent oxygen sensitive compound into extruded polymer films. Specifically, there is disclosed a process for thermal melting of oxygen-sensitive indicators into common packaging polymers used for commercial packaging of products, such as foods. The oxygen-sensitive indicators can be used for real-time monitoring of oxygen in commercial packaging operations.

PROCESS FOR FORMING POLYMER STRUCTURES CONTAINING AN OXYGEN SENSOR

Technical Field of the Invention

5 This invention provides a process for fabricating oxygen-sensing polymers and methods for measuring the oxygen contents of packages and containers. In particular, this invention provides a process for the preparation and use of flexible polymer films containing an oxygen sensitive indicator and the instrumentation for quantifying said package's oxygen contents.

Background of the Invention

10 There is a need for practical, economical, large-scale manufacturing and implementation of polymeric gas sensors with particular utility to the packaging industry. Packaging of oxygen sensitive foods, pharmaceuticals or medical supplies typically employs engineered gas barrier films and containers, inert gas flushes and high-speed heat-sealing equipment. There are no available technologies that provide a practical means for measuring in-package oxygen on a real
15 time basis. In addition to packaging, many potential applications for oxygen sensing inside containers would benefit from the use of low-cost and sensor-containing barrier polymeric films.

Oxygen monitoring inside containers has required destructive lot testing and laborious, gas-sampling techniques. One common method requires that a needle be inserted into the headspace of a package and an air sample withdrawn for analysis. This method is prone to
20 sampling errors, will result in loss of product (due to package integrity breach) and will provide only historical information rather than real-time data useful for process control. Therefore, there is a need for a non-invasive measurement method.

Optical sensors have been placed into a package and read via changes in absorbance, luminescent intensity or luminescent lifetime properties of the indicators. While these non-
25 invasive optical sensors offer potential advantages over physical sampling techniques, they pose numerous practical disadvantages and added per-test costs to implement. Commonly described optical gas-sensor designs are prepared by casting or painting polymers dissolved in an organic solvent containing gas sensitive optical indicators (e.g., porphyrins, ruthenium, pyrenes) onto a substrate, such as glass, plastic or paper. The sensor can either be prepared as a distinct sensing
30 coupon added to the package prior to sealing or it can be directly painted onto the inside surface of the package.

U.S. Patent 4,810,655 (Khalil) describes an optical sensor cast from a volatile organic solvent solution of indicator and a carrier polymer cast onto a suitable inert substrate. Due to the nature of most suitable organic solvents, direct printing or painting onto flexible packaging using
35 these sensor solutions has the potential for changing the engineered properties of these multilayer films including delamination, cracking, changes in film orientation and migration of processing additives. These problems provide significant hurdles to practical implementation of solvent-based casting, paint or printing methodologies. Other significant problems are inherent to

solvent use, such as, flammability of the solvents, hazardous waste storage and removal, and the elimination of toxic fumes for worker safety.

Solventless approaches to preparing sensor films have been described (U.S. Patents 4,657,736 and 5,407,829) by casting thin polymerizable films of ruthenium and a silicone copolymer onto food packaging films followed by completing the polymerization to form a sensor element. Although potentially minimizing effects on the packaging film and the other noted problems associated with solvent use, the equipment and logistics of applying and completing polymerization of the sensor material in the volumes necessary for the food packaging industry are well outside the common practice of film manufacturers. One further constraint to "painting" a sensor onto the overwrap material is the heat-sealing process used in most flexible packaging operations. Packaging films will have a sealing layer designed to provide a bond at specific parameters (*e.g.*, temperature, dwell time) for the packaging machine. Application of even a thin polymer film in the sealing area can result in poor heat seals and package failure. Therefore, any process using "painted" sensors would require more elaborate film production equipment and orientation of the film during packaging than is commonly found in the industry.

In addition to the difficulty with preparing a practical optical sensor, it also has been difficult to implement an instrument for field use. Lifetime methods provide advantages of internal signal referencing that compensate for changes in signal path and oxygen-sensitive indicator concentration. Two such methods are based on phase-modulation or time-resolved determination of the luminescent lifetime. Although phase-modulation based methods can provide precise measures of lifetime, for applications with low concentrations of oxygen-sensitive indicator and irregular surfaces or sensor configurations with inconsistent reflection properties, the time resolved method provides greater immunity from correlated stray light (excitation) that can lead to non-reproducible performance of the phase-based method.

The addition of pigments to color polymer extrusions has been practiced (*e.g.*, U.S. Patent 5,185,038). Phosphorescent coatings have been prepared using a continuous hot-melt method (U.S. Patent 3,873,390). Both methods use inorganic particles, luminescent or simply colored. In neither case is it suggested that these films would be useful optical gas sensing structures. Also common to patents for pigmenting polymers is the use of inorganic particles, luminescent or simply colored. As noted in Khalil (US 4801655), a key element to creating useful luminescent oxygen probes from organic indicators such as porphyrins and chlorins is the complete dissolution of the indicator in the polymer. The thermal melt processes taught by this patent utilizes a narrow window of gas-indicator thermal stability and polymer melt processing temperatures common to extrusion processes to form useful oxygen indicating structures.

Summary of the Invention

The present invention provides a process for manufacture of oxygen sensitive polymeric structures by the addition of an oxygen-sensitive indicator directly to the thermal melt phase of polymers during extrusion processes. Preferably, the oxygen-sensitive indicator is luminescent.

Importantly, the inventive process allows the integration of oxygen sensing functionality into polymer films, including multilayer barrier films common to the food packaging industry.

The present invention provides a process for making an oxygen-sensitive polymeric structure, comprising

5 (a) adding an oxygen-sensitive indicator to a thermoplastic polymeric material heated to just above its melting temperature;

(b) mixing the oxygen-sensitive indicator thoroughly within the thermoplastic polymeric material while continuing the heating to maintain the thermoplastic polymeric material in a substantially liquid form; and

10 (c) forming the mixture into an end product form of indicator-polymer product.

Preferably, the forming step is accomplished by an extrusion process, a molding process or an injection molding process. Preferably, the oxygen-sensitive indicator is selected from the group consisting of polycyclic aromatic hydrocarbons, pyrene, fluoranthene, decacyclene, diphenylanthracene, benzo(g,h,i)perylene), porphyrins, platinum or palladium
15 octaethylporphyrin, tetraphenylporphyrin, tetrabenzporphyrin, chlorins, bacteriochlorins, isobacteriochlorins, chlorophyll), and combinations thereof. Preferably, the polymeric material is selected from the group consisting of linear ethylene alpha olefin copolymers, ethyl vinyl acetate, linear low-density polyethylene (LLDPE), very-low-density polyethylene (VLDPE), metallocene catalyzed polymers, and combinations thereof. Preferably, the melting temperature
20 is from about 140 °C to about 240 °C.

The present invention further provides a multi-layered food packaging film having an ability to detect oxygen presence within a packaging, comprising an indicator polymer product film and a plurality of non-oxygen sensing polymer films bonded thereto, wherein the indicator polymer product is made by a process comprising:

25 (a) adding an oxygen-sensitive indicator to a thermoplastic polymeric material heated to just above its melting temperature;

(b) mixing the oxygen-sensitive indicator thoroughly within the thermoplastic polymeric material while continuing the heating to maintain the thermoplastic polymeric material in a substantially liquid form; and

30 (c) forming the mixture into an end product form of indicator-polymer product.

Preferably, the forming step is accomplished by an extrusion process, a molding process or an injection molding process. Preferably, the oxygen-sensitive indicator is selected from the group consisting of polycyclic aromatic hydrocarbons, pyrene, fluoranthene, decacyclene, diphenylanthracene, benzo(g,h,i)perylene), porphyrins, platinum or palladium
35 octaethylporphyrin, tetraphenylporphyrin, tetrabenzporphyrin, chlorins, bacteriochlorins, isobacteriochlorins, chlorophyll), and combinations thereof. Preferably, the polymeric material is selected from the group consisting of linear ethylene alpha olefin copolymers, ethyl vinyl acetate, linear low-density polyethylene (LLDPE), very-low-density polyethylene (VLDPE), metallocene catalyzed polymers, and combinations thereof. Preferably, the melting temperature

is from about 140 °C to about 240 °C. Flexible polymeric materials commonly used to form oxygen barrier layers include poly(ethylene vinyl alcohol) (EVOH), polyacrylonitrile, polyvinyl chloride, poly(vinylidene dichloride), polyethylene terephthalate, polyamides, or combinations thereof. Preferably, the indicator polymer product is coextruded or laminated to one or more of these barrier-forming materials during manufacture of the film.

Brief Description of the Drawings

Figure 1a shows a laboratory instrument for determination of Stern-Volmer relationships. Specifically, the optical instrument consists of a (1) 50W Tg-Halogen source, (2) optical excitation filter(s), (3) collimation optics, (4) beam-splitter, (5) focusing optics, (6) target, (7) emission filters, (8) PMT and amplifier, and (9) a CPU for data collection and control.

Figure 1b shows examples of Stern-Volmer responses for PtTPP and PdTPP oxygen sensitive indicators dissolved in a LLDPE film (prepared as described in the examples section). Figure 1b illustrates differences in responsivity engendered by two types of oxygen-sensitive indicators when used with the same polymer. Specifically, Figure 1b shows the greater oxygen responsiveness of the PtTPP indicator-polymer signal in the range of 21% oxygen (room air) to approximately 1% oxygen when compared to the PdTPP indicator-polymer. In the lower oxygen ranges from 1% to less than 0.01%, the PdTPP indicator-polymer demonstrates a greater change in luminescent intensity (and lifetime) than the PtTPP indicator-polymer.

Figure 2a shows the instrumentation components of the optical system used for making ratiometric luminescence lifetime measurements of oxygen sensitive indicator-polymer films.

Figure 2b shows an example of the luminescent ratio response as a function of oxygen concentration. PdTPP indicator was dissolved in an LDPE polymer film at $0.6\mu\text{g}/\text{cm}^2$ using thermal methods (as described in more detail in the examples below). The oxygen-sensitive film was placed in the gas-flush chamber and measured optically at oxygen levels ranging from 0% to 1.1% O_2 /balance N_2 .

Figure 3 shows a representative emission spectra (excitation at 400nm) for a master batch of indicator polymer. The spectra of films are identical in their excitation and emission peaks to the dye in solution, indicating no thermal damage to the oxygen sensitive indicator during the polymer-indicator preparation.

Figure 4 shows the oxygen response results of three press-plaque sample films analyzed using the ratiometric lifetime instrumentation (of Figure 2a) and gas-flush test system as described herein. The ratio response curves over the oxygen concentration ranges of 0% to 0.7% oxygen (0-700ppm) for these three press-plaques are shown.

Figure 5 shows the PtTPP indicator-polymer's luminescent lifetime as a function of oxygen concentration. Lifetime measurements of the film were made inside a gas flushed test vessel using a "ratiometric" lifetime instrument over oxygen concentrations ranging from 21% to 0%. The maximal ratio change is in the 0.5% to 5% oxygen concentration range. This is contrasted with the Pd-based indicators described in Example 2 that have a maximal ratio change in the 0% to 1% oxygen concentration range.

Figure 6 shows that an indicator-polymer film in a multilayer laminate configuration - (see Example 5). The film responds to changes in oxygen concentration and does so to essentially the same level (ratio) as the indicator-polymer film as a monolayer. Figure 6 also shows "Laminate-b", the ratio response of the indicator-polymer laminated to an LLDPE film that in turn is laminated between two gas-barrier films.

Detailed Description of the Invention

The present invention is an improved process for forming films having an oxygen-sensitive indicator dissolved directly into the thermally melted polymer phase common to plastic extrusion processes. The indicator-polymer product can then subsequently be shaped in a thermal melt form to fabricate oxygen-sensory structures of desired configuration via extrusion or molding processes (e.g., injection molding). Alternatively, the indicator-polymer can be cut, skived or otherwise mechanically machined into a desired configuration by manufacturing processes practiced in the plastics industry. A preferred embodiment is to fabricate the indicator-polymer in a thin film form with the objective of promoting rapid transfer of gas through the material.

The inventive process provides particular utility and economy towards fabrication of films used for packaging including multi-layer laminates and coextruded films containing the indicator-polymer material in at least one layer of these films, for example, with extrudable polymers and copolymers useful in the packaging field including, for example, linear ethylene alpha olefin copolymers such as ethyl vinyl acetate, LLDPE, VLDPE, and metallocene catalyzed polymers. In addition to films, other polymer shapes can be made, such as, caps, cap liners, lids, bottles, and rigid containers that incorporate the oxygen-sensitive indicator. Preferably, the oxygen-sensing indicator is luminescent. Most preferably, the oxygen-sensitive indicator is selected from the group consisting of polycyclic aromatic hydrocarbons (i.e., pyrene, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene), porphyrins (i.e., platinum or palladium octaethylporphyrin, tetraphenylporphyrin, tetrabenzporphyrin, chlorins, bacteriochlorins, isobacteriochlorins and chlorophyll), and combinations thereof. A common characteristic of these oxygen-sensitive indicators is solubility in the thermal-melt polymers such as those used in flexible film packaging. Furthermore, the oxygen-sensitive indicators are thermally stable at the temperatures required for thermoplastic fabrication. Complexes such as ruthenium(II)tris(bipyridyl) complexes, osmium (II)tris(bathophenanthroline) are not ideal candidates due to their poor solubility in the polymer melt.

Preferred oxygen-sensitive indicators include platinum (Pt) and palladium (Pd) chelate derivatives of octaethyl porphine (PtOEP & PdOEP respectively), and similarly Pt- & Pd-tetraphenyl porphine (PtTPP & PdTPP), and Pt- & Pd-tetrafluoro porphine (PtTFPP & PdTFPP). The PtTPP & PdTPP oxygen-sensitive indicators have advantages in cost. Additionally, they have low solubility in typical extraction test conditions important for compliance with FDA and USDA safety guidelines regarding extractables. The TFPP oxygen-sensitive indicators have

oxidation stability (primarily photooxidation) and are useful for long-term storage and monitoring of oxygen packaging applications.

Luminescent Indicator	Lifetime millisec	% Quantum Yield	Optimal Oxygen Range	Other
PtOEP	0.13	90%	21% - 1%	
PdOEP	1.96	50%	2% - 0.005%	
PtTPP	0.25	45%	21% - 1%	more stable to
PdTPP	2.0	20%	2% - 0.005%	oxidation than
				OEP – low cost
PtTFPP	0.12	50%	21% - 1%	greater stability than TPP

5 The optimal ranges of oxygen measurements depend upon the associated metal ligand. Platinum ligands, with natural decay lifetimes of 70-100 μ s, are useful for determining oxygen concentrations in the range of 21% to 1%. Palladium ligand indicators, such as PdTPP, have natural decay lifetimes greater than 1 ms and are useful for determination of oxygen concentrations below 2%. Hafnium chelates can provide even lower oxygen sensitivities.

10 The thermal melt of the indicator-polymer can be further processed in any of a number of ways, including mixing and dilution with more of the same base polymer; mixing with other polymers; coextrusion with the same or other polymers; extrusions as a film; incorporation as a film with other layers of films to form multilayered products. In the case of multilayered products, the different layers are designed to provide particular functionalities, such as, adhesive layers to provide bonding properties. In a preferred embodiment for packaging applications to determine the oxygen within a sealed environment, a thin film indicator polymer layer made by the inventive process is incorporated into a package or vessel lidding material having an outer oxygen barrier layer, and additionally juxtaposed on the side internal to the package, an oxygen-permeable food safe contact layer.

20 In one embodiment, the oxygen-sensing characteristic of the polymer product, or the oxygen in an environment, is visually ascertained by placing a thin piece of indicator-polymer film into an environment wherein the oxygen content is to be sensed. The color characteristic or luminescent properties of the oxygen-sensitive indicator change in an oxygen dependent manner. By irradiating the polymer product with light (electromagnetic radiation) of appropriate spectral characteristics one can visually ascertain the response of the polymer product to the oxygen present.

25 Alternatively, one can measure the oxygen in the environment in which the indicator product is placed using optical instrumentation. In this scenario, electromagnetic radiation is

directed at the polymer product. A signal of electromagnetic radiation returned by the polymer product containing an oxygen-sensitive indicator is captured by an optical detector. The intensity of the return signal and its luminescent lifetime change in an oxygen concentration dependent manner.

5 Instrumentation for Intensity-Based Luminescent Signal Measurements of Oxygen

A laboratory instrument for determination of Stern-Volmer relationships is shown in Figure 1a. The optical instrument consists of a (1) 50W Tg-Halogen source, (2) optical excitation filter(s), (3) collimation optics, (4) beam-splitter, (5) focusing optics, (6) target, (7) emission filters, (8) PMT and amplifier, and (9) a CPU for data collection and control. The
10 sample of indicator-polymer is held in a gas-tight chamber connected to a vacuum pump. An electronic pressure gauge measures the chamber pressure. The computer initiates a measurement cycle at atmospheric pressure (21% oxygen) and records the luminescent intensity as a function of the gauge pressure. The vacuum system modulates the pressure and thereby the oxygen content that the sample is exposed to within the chamber vessel.

15 The resulting data are plotted in a Stern-Volmer relationship (I/I_0 vs $\ln(P)$ where I_0 is the intensity measured with no oxygen quenching) to determine the characteristic response of the indicator-polymer to decreasing oxygen concentration. Examples of Stern-Volmer responses for PtTPP and PdTPP oxygen sensitive indicators dissolved in a LLDPE film (prepared as described in the examples section) are shown in Figure 1b. Figure 1b illustrates differences in responsivity
20 engendered by two types of oxygen-sensitive indicators when used with the same polymer. Specifically, Figure 1b shows the greater oxygen responsiveness of the PtTPP indicator-polymer signal in the range of 21% oxygen (room air) to approximately 1% oxygen when compared to the PdTPP indicator-polymer. In the lower oxygen ranges from 1% to less than 0.01%, the PdTPP indicator-polymer demonstrates a greater change in luminescent intensity (and lifetime) than the
25 PtTPP indicator-polymer.

For oxygen levels above 5%, the low luminescent intensity of the Pd-indicators requires high gain PMT photodetectors, precision optics and attention to minimizing stray light to reliably measure the small luminescent signal. For example, measuring Pt-indicators at moderate oxygen levels of 10% requires a PMT voltage of 400V compared to the Pd-indicator minimum of 900V
30 (a gain difference of over 10^3). The ability to select the most appropriate indicator based on the application's anticipated oxygen concentration is critical to the design of instrumentation optimally suited both financially and design wise for the industrial setting. This example also serves to illustrate the use of indicator-polymer to ascertain the pressure, or change of pressure in an environment, based on the measurement it yields of the oxygen content.

35 Instrumentation for Luminescent Lifetimes

The instrument shown in Figure 2a provides for ratiometric measurement of luminescent lifetime in a time domain. As a general instrument format, a light source modulated as a step function at a fixed frequency between 200 and 1500 Hz is focused onto the indicator-polymer test film sample (15) to excite the luminescent indicator molecules. The luminescent light from

the indicator is collected by condensing optics and focused onto a photodetector. The signal is analyzed to determine its characteristic lifetime.

In a preferred format, an optical head (10) contains solid state light sources (11) (Nichia *NLPB 500* LED - center wavelength at 450nm) and focusing optics (12) and a detector (13) (Burr-Brown OPT210 high-speed integrated PIN-amplifier) are used. These parts are integrated in a hand-held optical head that is connected to the Ratiometric Lifetime Analyzer board (14). After compensating for low frequency ambient light, the Ratiometric Lifetime Analyzer estimates the luminescent signal's lifetime by integrating the electronic signal from two consecutive time periods during the signal decay (I_1 & I_2) and calculating the ratio of these two return intensities (I_2 / I_1). The signal ratio is determined by a 12 bit A/D and output as a number from 1 to 4095. In this scheme, as the lifetime increases, the ratio of the two intensities increases. For the luminescent indicators quenched by oxygen, as the oxygen concentration goes down, O_2 quenching decreases, the luminescent lifetime increases and the ratio of I_2/I_1 increases as well. By adjusting the periods of I_1 and I_2 , the instrument can be optimized for indicators with widely differing luminescent lifetimes and for any unique characteristics of the indicator-polymer.

In the preferred mode of use, the oxygen-sensitive indicator is present in the polymer product at concentrations imperceptible to the unaided eye (typically $0.155 \mu\text{g}/\text{cm}^2$). Long integration times for the two consecutive time periods provides reproducible measurements for luminescent quenching in films containing very low concentrations of oxygen-sensitive indicator.

In general, a luminescent indicator-polymer's oxygen response was measured by placing a sample of it, preferably in the form of a film, in the window of a gas-flushed chamber. A Mocon oxygen analyzer, placed in line with the flush gas, provided a measure of the oxygen content in the chamber. The flush gas was modulated to yield different concentrations of oxygen such that the luminescent ratio responsive of the indicator-polymer sample can be measured at multiple known oxygen concentrations. An example of the luminescent ratio response as a function of oxygen concentration is shown in Figure 2b. PdTPP indicator was dissolved in an LDPE polymer film at $0.6 \mu\text{g}/\text{cm}^2$ using thermal methods (as described in more detail in the examples below). The oxygen-sensitive film was placed in the gas-flush chamber and measured optically at oxygen levels ranging from 0% to 1.1% O_2 /balance N_2 . The signal ratio as a function of the percentage of oxygen concentration is shown in Figure 2b.

Example 1

This example provides a process for producing a polymer-indicator product with commercial utility as a colorant masterbatch. Color concentrates are high-content mixtures of dye in a carrier resin most commonly used for coloration of a polymer film, sheet or molded part. Color concentrates or masterbatches, are mixed with process polymers to prepare colored parts. In this example, we describe methods for preparation of 3-different colorant masterbatches.

100 Grams of a polyethylene-octene copolymer (Elite 5100, Dow Chemical) was added to the mix chamber of a Braebender mixer and melted at a temperature of 200 °C for approximately 5 minutes. One-gram of oxygen sensitive indicator (PtOEP) (Strem) was added to the polymer melt and mixed for an additional 7 minutes. The chamber was cooled to room
5 temperature and the hardened polymer product was removed. Visual examination of the batch showed a homogeneously mixed material with no inclusions or exclusions of oxygen sensitive indicator noted. Fluorescence excitation and emission spectra of the material were measured using a SPEX Skin-Scan Fiber Optic Fluorometer at excitation wavelengths from 380nm to 540nm and emission wavelengths from 550nm to 750nm. A representative emission spectrum
10 (excitation at 400nm) is shown in Figure 3. The spectra of films are identical in their excitation and emission peaks to the dye in solution, indicating no thermal damage to the oxygen sensitive indicator during the polymer-indicator preparation. The product material (designated as PtOEP-Masterbatch #1) was chopped and used for production of test films as described in later examples.

15 In addition, a small-sample masterbatch was prepared by melting 5 grams of a linear low density polyethylene (Dowlex 2245, Dow Plastics) at 230 °C in a glass vessel and mixing 17 mg of PdTPP [Strem] into the polymer melt by hand until solubilization and blending was complete according to a visual examination. Again, no discoloration or indication of thermal damage was noted and fluorescence spectra showed no unexpected peaks. The product material (designated
20 as PdTPP-Masterbatch #2) was chopped and used for production of test films as described in later examples.

A third masterbatch of indicator-polymer was prepared using a Rand-Castle Tabletop twin screw mixer-extruder by mixing 3-grams of oxygen sensitive indicator (PdTPP) to a process stream of a linear low-density polyethylene (Dowlex 2245, Dow Chemical). The final mix ratio
25 of indicator to polymer was approximately 3:4,200 (w/w). Extruded indicator-polymer showed no visual or fluorescence excitation/emission spectra evidence of thermal degradation. This final example demonstrates methods that might be commercially useful for preparation of colorant masterbatches. It should be recognized by those practiced in the art that other thermal melt methods and machinery for preparing colorant masterbatches are to be included.

30 Example 2

This example illustrates compounding polymer masterbatch products into carrier polymers including LLDPE's normally used in the manufacture of food packaging films. LLDPE refers to linear low-density polyethylene and copolymers of ethylene with one or more comonomers selected from preferably C4 to C10 alpha olefins such as octene. Commercially
35 available examples of these include: Elite 5100 – an ethylene-octene copolymer (Dow Plastics); Dowlex 2245 – a low-density polyethylene (Dow Plastics). Rexene Pe1375 is an ethylene-vinyl acetate copolymer (Huntsman).

A 100-mg sample of PdTPP Masterbatch #2 was diluted by blending into 3 grams of undyed carrier polymer (ethylene-octene copolymer, Elite 5100). Pellets of the two materials

were melted in a vessel heated to 200 °C and mixed thoroughly by hand for 4 minutes. The mixture was cooled to room temperature and the indicator-polymer was removed and cut into small pieces, each piece weighing approximately 100 mg each. A sample of the indicator-polymer mixture was subsequently reheated to 200 °C and pressed between two glass plates to form a thin film "press-plaque" approximately 1-2mil thick. The final indicator concentration in the press plaque was approximately 0.6µg/cm².

Press-plaques were also made using the PdTPP Masterbatch #2 mixed into the commercial polymers, Rexene and Dowlex 2245. Identical procedures as described above were used, substituting the Rexene or Dowlex polymers for the carrier polymer. In each of these cases, the final indicator concentration is estimated at 0.6 µg/cm² in the press-plaques.

The three press-plaque sample films were analyzed using the ratiometric lifetime instrumentation and gas-flush test system described herein. The Ratio response curves over the oxygen concentration ranges of 0% to 0.7% oxygen (0-700ppm) for these three press-plaques are shown in Figure 4. These results in this figure demonstrate that the Ratio characteristics of the different polymer-indicator combinations differ slightly, as might be expected from the oxygen solubility differences between the three carrier polymers. However, any of these would be a suitable candidate for use in an oxygen-sensing layer of a laminate or multilayer film.

Example 3

This example demonstrates the production of an extruded polymer film containing the indicator in a single layer of the extruded film. 100 grams of the PtOEP Masterbatch #1 (indicator-polymer) pellets prepared in Example 1 were added to the second hopper of a Rand-Castle Tabletop extruder. The process chamber temperature was maintained at 205 °C. The polymer materials were calculated to have a 3-5 minute mean residence time in the extruder. The masterbatch material was mixed into a process stream of the commercial polymer, Elite-5100, in the extruder from which a film was extruded (3/4ft x 100ft x 2mil). The final indicator concentration of in the film was approximately 0.3µg/cm². No signs of inclusions or gels or other anomalies were found thus indicating that the presence of the indicator did not create interferences with the extrusion process.

The film had a slightly pink hue that visibly became brighter when placed in a low oxygen environment and illuminated with a "black-light". Coloration from the indicator was uniform throughout the 100-foot web of film. Luminescence intensity measurements were made at 10 separate areas along the film length, including the first and last foot of film, using the instrumentation described herein (Figure 1a). Each of these measures demonstrated uniform oxygen responsivity along the web. Similarly, fluorescence spectra of the film were similar to each other and similar to spectra of the dye itself. Lifetime measurements of the film were made using the ratiometric lifetime instrumentation and gas-flush oxygen test vessel described herein and in Figure 2b. The ratio response as a function of oxygen concentration (from 21% to 0%) is shown in Figure 5. In Figure 5, the maximal ratio change is in the 0.5% to 5% oxygen

concentration range. This is contrasted with a the Pd-based indicators described in Example 2 that have a maximal ratio change in the 0% to 1% oxygen concentration range.

These results show that indicator-polymer films prepared by extrusion are consistent along their length with respect to oxygen sensing and that the thermal processing parameters found in this extruder does not cause degradation of the indicator's oxygen sensing performance. Further, this example shows the utility of a PtOEP indicator polymer for measuring oxygen concentrations over the range of 21% to 1% oxygen.

Example 4

This example describes visual sensing of oxygen responses. Indicator polymers produced in Example 1 were extruded into press plaque films made as described in Example 2. Sample pieces were placed into an environment where exposure to oxygen was modulated in the gas-flush test chamber described herein (Instrumentation for Luminescent Lifetimes). Directing light from a Blacklight (GE, F15T8-BLB) at the thin film samples containing approximately $0.3\mu\text{g}/\text{cm}^2$ of the Pt-porphyrin indicators (PtTPP or PtOEP), the indicator-polymers were visually seen to luminesce when exposed to ambient air (21% oxygen). The luminescent intensity increased visibly as the indicator polymers were exposed to decreasing concentrations of O_2 (21% to 1%) in the flush gas. The luminescence was clearly discernible at all oxygen concentrations and the displacement of oxygen could be visualized by the perceptible increase in the indicator-polymer film's intensity over the entire oxygen concentration range.

On the other hand, film samples prepared with the PdTPP indicator (PdTPP Masterbatches #2 and #3) similarly viewed under Blacklight illumination were thoroughly quenched by exposure to low oxygen concentrations of even a few percent such that no luminescence was visible to the eye. Before exhibiting visually discernable luminescence, the oxygen concentration had to be reduced to ~1% or less. Thereafter, the intensity visibly increased the lower the oxygen level was driven by the N_2 flush gas. This example demonstrates that the oxygen-sensitive indicator-polymer provides means to visually sense the oxygen content and changes in oxygen in the environment in which it is placed.

Additionally, the thin film indicator-polymer samples described were exposed in air to flowing streams of N_2 flush gas blown through a nozzle directed at the samples. It was visually distinguishable, under Blacklight illumination, that the luminescence engendered was most intense at the center of the nitrogen gas directed stream. The intensity diminished in an oxygen concentration dependent manner the further the distance radially from the center point. These examples thus further demonstrate that the indicator polymer provides means to identify the presence or locale of leaks in an environment in either of two manners: via oxygen's escape causing quenching in a low-oxygen environment; or via escape of non-quenching gas, such as N_2 or CO_2 , into an oxygen rich environment thereby causing localized displacement of the oxygen quencher.

Example 5

This example provides the results from testing multilayered film structures made as laminates containing a layer of indicator-polymer and an oxygen-barrier. The indicator-polymer used in this example was PtOEP-Dowlex 2245. It was in the form of a thin film, made as an extruded press plaque from PtOEP Masterbatch #1, as described in Example 2.

In a first test, the indicator-polymer film was loosely taped at its edges to the window of the gas-flush test chamber described herein (Instrumentation for Luminescent Lifetimes). Nitrogen was flushed into the gas-flush test chamber and the change in the signal ratio of the indicator-polymer film was measured as a function of time. The results are shown in Figure 6 as "Film-Alone". The sensor responded quickly to a N₂ flush, reaching 95% of its final value within 60 seconds. This illustrates the capability of the indicator-polymer film when used by itself as a monolayer, to measure oxygen within the environment to which it is exposed.

Following this test, the indicator-polymer film was heat laminated to a multilayer oxygen-barrier flexible wrap film obtained from a commercially available modified-atmosphere food package ("Ready Crisp Bacon", SHK, Inc.). To laminate, the package oxygen-barrier film was placed on a hot-plate with its food-contact layer's surface facing up and the indicator-polymer film was placed on this surface. The two films were lightly pressed together and heat bonded to one another eliminating bubbles and wrinkles to form multilayer laminate-a. The laminate-a was tested using the gas-flush test chamber previously described, but in this case the chamber was modified by removing the glass window from the port used for optical interrogation of the sample within. Laminate-a was mounted in the open port of the modified gas-flush test chamber such that the indicator-polymer film was exposed internally to the gas contents inside the chamber. The opposing side of laminate-a, bearing the oxygen-barrier film, was externally exposed to ambient air. The gas-flush test chamber was purged with nitrogen flush gas.

The result shown in Figure 6 demonstrates that the indicator-polymer film in the configuration of multilayer laminate-a still responded to changes in oxygen concentration and did so to essentially the same level (ratio) as the indicator-polymer film when by itself as a monolayer (the first test above). As expected, the response time characteristic of the indicator-polymer film in the laminate configuration was slower than by itself as a monolayer since the multilayer oxygen-barrier film impedes oxygen transfer via its bonded side. Nonetheless, the example shows that the indicator-polymer film in the laminate retains response characteristics similar to its monolayer form and would serve to measure the internal oxygen contents of a package or vessel.

Also shown in Figure 6 as "Laminate-b" is the response of the indicator-polymer film in the laminated configuration last described above, but in this case the indicator-polymer film was further covered on its exposed surface with a layer of "Scotch-tape" adhered over it – a relatively gas impermeable barrier material. In this configuration, laminate-b, the indicator-polymer film layer was thereby "sandwiched" between the multilayer oxygen-barrier film and the tape that is

obstructing its exposure to the environment to be sensed. The laminate-b sample was attached to the open port of the gas-flush test chamber in the same manner as the previous laminate test example and the chamber purged with nitrogen gas while monitoring the indicator-polymer film's signal response. The results indicate that the indicator-polymer film in laminate-b configuration registered a lower ratio, indicating a higher oxygen concentration within the indicator-polymer film layer, than observed on the previous films' tests at equivalent times throughout the test period (over 1600 seconds). This last example serves to illustrate that the indicator-polymer can be used for not only measuring the internal package oxygen contents, but also the kinetics of oxygen within film structures. Because the indicator can be placed in most, if not all the film's internal layers, this feature is exploitable to usefully measure the oxygen permeation rates through various film layers and different polymers. Furthermore, by continuous monitoring of change in oxygen within a structure, valuable insights regarding active processes occurring internally in the film (*e.g.* hydration, decomposition, oxygen scavenging) are gained.

Example 6

The curve labeled "Delam" in Figure 6 shows the result of peeling apart the film layers in the multilayer laminate-b, and retesting the indicator-polymer film by itself again loosely fixed to the glassed window of the gas-flush test chamber as was done in the first case of Example 5. As observed, the delaminated indicator-polymer film in the repeat test demonstrated essentially the same response characteristics as shown previously. This indicates that the indicator-polymer oxygen response characteristic remained consistent and that the results of the various test sample configurations were due to the nature of the various structures and not an intrinsic change in the indicator-polymer film.

Example 7

The indicator-polymer film of Example 5 was heat laminated by itself directly onto the gas-flush test chamber's glass window that represents a highly efficient oxygen-barrier material that contains negligible oxygen. The chamber was purged with nitrogen gas and the change in the signal ratio of the indicator-polymer film measured as a function of time in the same manner performed in Examples 5 and 6. The results are presented as "glass-lam" in Figure 6. As expected the indicator-polymer film in the glass-lam configuration was slower to respond to oxygen change in contrast to the indicator-polymer film by itself (see Example 6 "delam", and the "film alone" of Example 5, indicated in Figure 6). The glass-lam results were similar to those shown for the Bacon package's oxygen-barrier film laminate with the indicator-polymer (laminate-b of Example 5); albeit perhaps the glass-lam's response to nitrogen flushing was slightly faster, perhaps since glass does not harbor entrapped oxygen that would slow the response. Comparison of the glass-lam, laminate-b and indicator-polymer "film alone" results suggest that an important factor in the response times of the films (although not their equilibrium responses) is the diffusion area, *i.e.* whether film is exposed on both sides, or only on one side, to the gas environment. Further, though, these results show that the indicator-polymer film response is modulated by the oxygen content surrounding it.

Example 8

This example describes how the process of melting an indicator into a polymer can serve to demonstrate that melting, or thermal bonding, such as in heat sealing operations, has occurred. PtTFPP indicator was dissolved into methanol at 50ug/ml. Two press-plaque films of Dowlex 2245 were prepared, as described in Example 2, but without incorporating indicator into the polymer melt. The PtTFPP indicator solution was administered to the surface of one plaque and allowed to evaporate. Since the methanol did not dissolve the Dowlex polymer, the indicator was left deposited as a coating on the surface of the plaque at a concentration of approximately 4ug/cm². The indicator coating in this state exhibited no visible luminescence when examined under a Blacklight (as described in Example 4) even when exposed to a N₂ gas flush.

The plaque surface with the indicator coating was overlaid with the other Dowlex press-plaque film also made without indicator, such that the coating was sandwiched between the two polymer film pieces. A portion of the two-plaque sandwich was exposed to localized heating to 230 °C, sufficient to melt and bond the two plaques together at the region where the heat was applied. Visual examination of the melted region under the Blacklight revealed that indicator luminescence could be seen, but only in the bonded region of the press-plaques. Luminescence could not be distinguished where melting and bonding did not occur.

We claim:

1. A process for making an oxygen-sensitive polymeric structure, comprising
(a) adding an oxygen-sensitive indicator to a thermoplastic polymeric material heated
to just above its melting temperature;

5 (b) mixing the oxygen-sensitive indicator thoroughly within the thermoplastic
polymeric material while continuing the heating to maintain the thermoplastic polymeric
material in a substantially liquid form; and

(c) forming the mixture into an end product form of indicator-polymer product.

2. The process for making an oxygen-sensitive polymeric structure of claim 1
10 wherein the forming step is accomplished by an extrusion process, a molding process or an
injection molding process.

3. The process for making an oxygen-sensitive polymeric structure of claim 1
wherein the oxygen-sensitive indicator is selected from the group consisting of polycyclic
aromatic hydrocarbons, pyrene, fluoranthene, decacyclene, diphenylanthracene,
15 benzo(g,h,i)perylene), porphyrins, platinum or palladium octaethylporphyrin,
tetraphenylporphyrin, tetrabenzporphyrin, chlorins, bacteriochlorins, isobacteriochlorins,
chlorophyll), and combinations thereof.

4. The process for making an oxygen-sensitive polymeric structure of claim 1
wherein the polymeric material is selected from the group consisting of linear ethylene alpha
20 olefin copolymers, ethyl vinyl acetate, LLDPE, VLDPE metallocene catalyzed polymers, and
combinations thereof.

5. The process for making an oxygen-sensitive polymeric structure of claim 1
wherein the melting temperature is from about 140 °C to about 240 °C.

6. A multi-layered food packaging film having an ability to detect oxygen presence
25 within a packaging, comprising an indicator polymer product film and a plurality of non-oxygen
sensing polymer films bonded thereto, wherein the indicator polymer product is made by a
process comprising:

(a) adding an oxygen-sensitive indicator to a thermoplastic polymeric material heated
to just above its melting temperature;

30 (b) mixing the oxygen-sensitive indicator thoroughly within the thermoplastic
polymeric material while continuing the heating to maintain the thermoplastic polymeric
material in a substantially liquid form; and

(c) forming the mixture into an end product form of indicator-polymer product.

7. The multi-layered food packaging film of claim 6 wherein the forming step is
35 accomplished by an extrusion process, a molding process or an injection molding process.

8. The multi-layered food packaging film of claim 6 wherein the oxygen-sensitive
indicator is selected from the group consisting of polycyclic aromatic hydrocarbons, pyrene,
fluoranthene, decacyclene, diphenylanthracene, benzo(g,h,i)perylene), porphyrins, platinum or

palladium octaethylporphyrin, tetraphenylporphyrin, tetrabenzporphyrin, chlorins, bacteriochlorins, isobacteriochlorins, chlorophyll), and combinations thereof.

9. The multi-layered food packaging film of claim 6 wherein the polymeric material is selected from the group consisting of linear ethylene alpha olefin copolymers, ethyl vinyl acetate, LLDPE, VLDPE metallocene catalyzed polymers, and combinations thereof.

10. The multi-layered food packaging film of claim 6 wherein the melting temperature is from about 140 °C to about 240 °C.

Figure 1a

Intensity Instrumentation for Stern-Volmer Characterizations – optical and vacuum measurement system

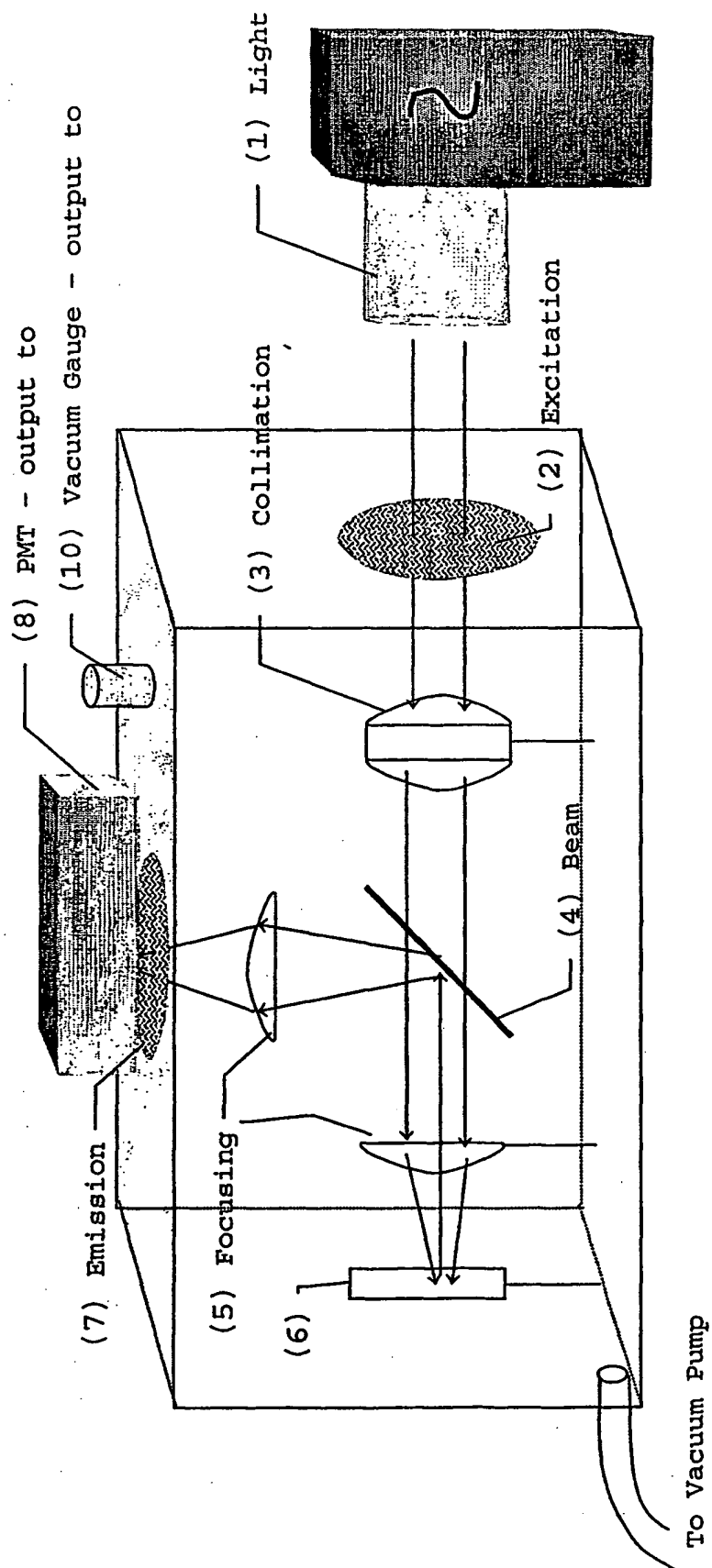


Figure 1b
Comparison of Stern-Volmer Response Characteristics for PtTTP and PdTTP in LDPE Film
ethylene-octene copolymer

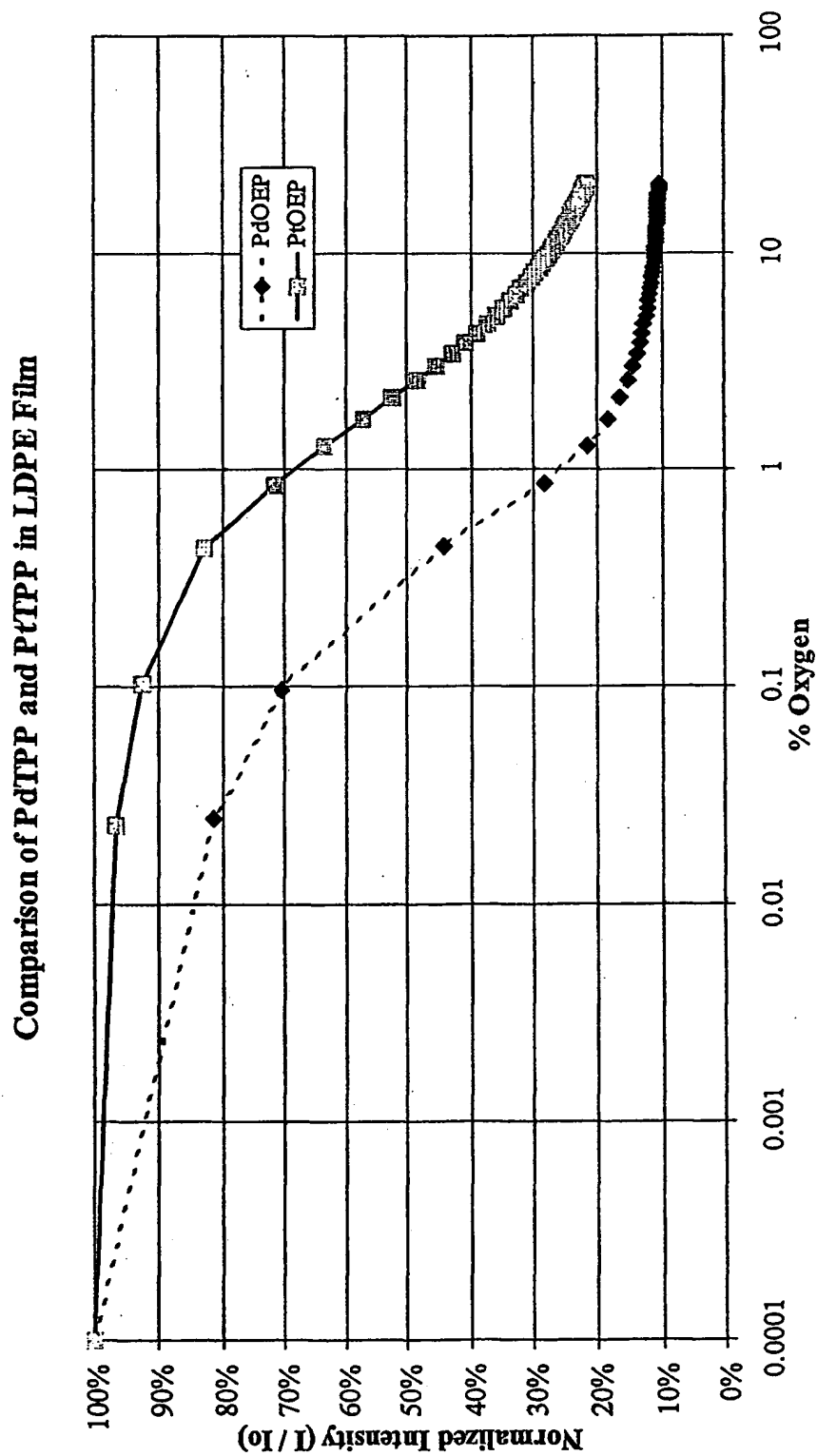


Figure 2a

Optical instrumentation used for lifetime measurements

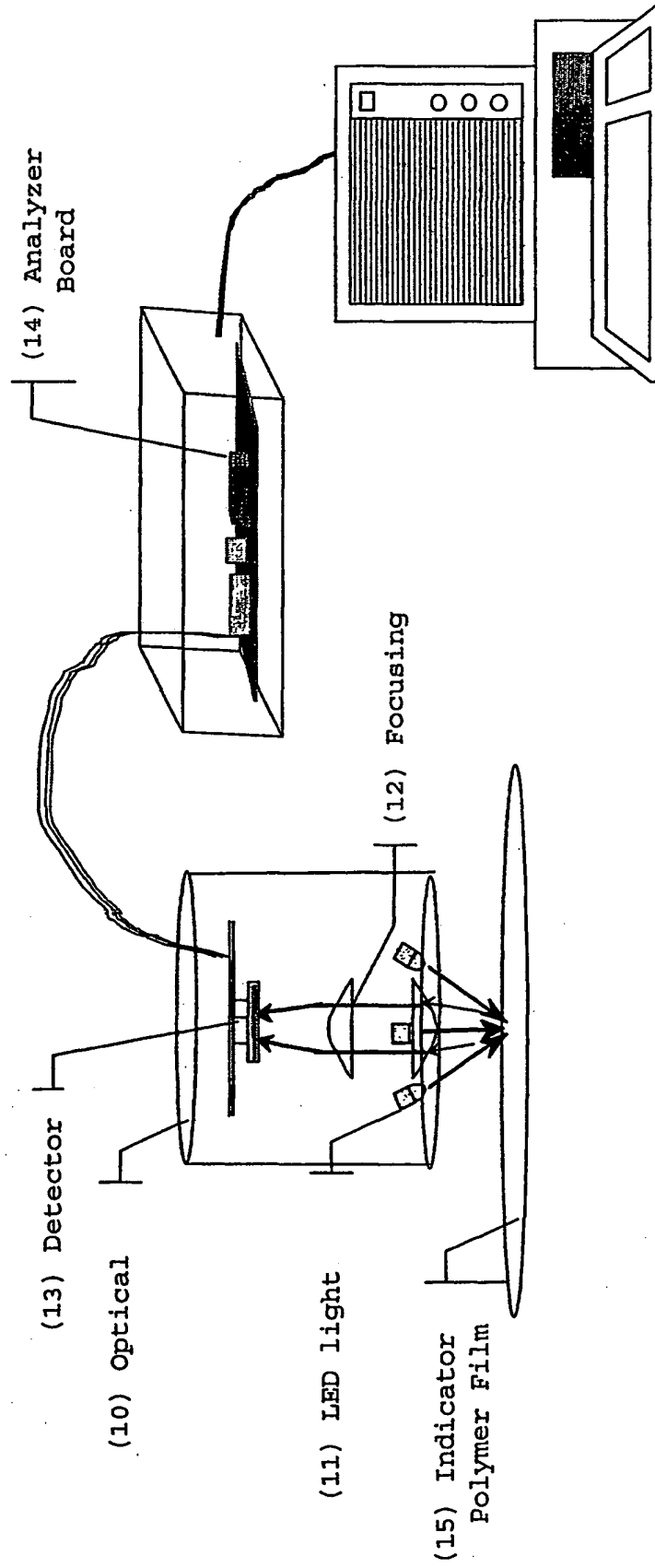


Figure 2b

Ratio Response of PdTPP Dye in LDPE as a Function of Oxygen Concentration.

Ratio Response of PdTPP Indicator-Polymer Using Lifetime Instrumentation
PdTPP in LDPE

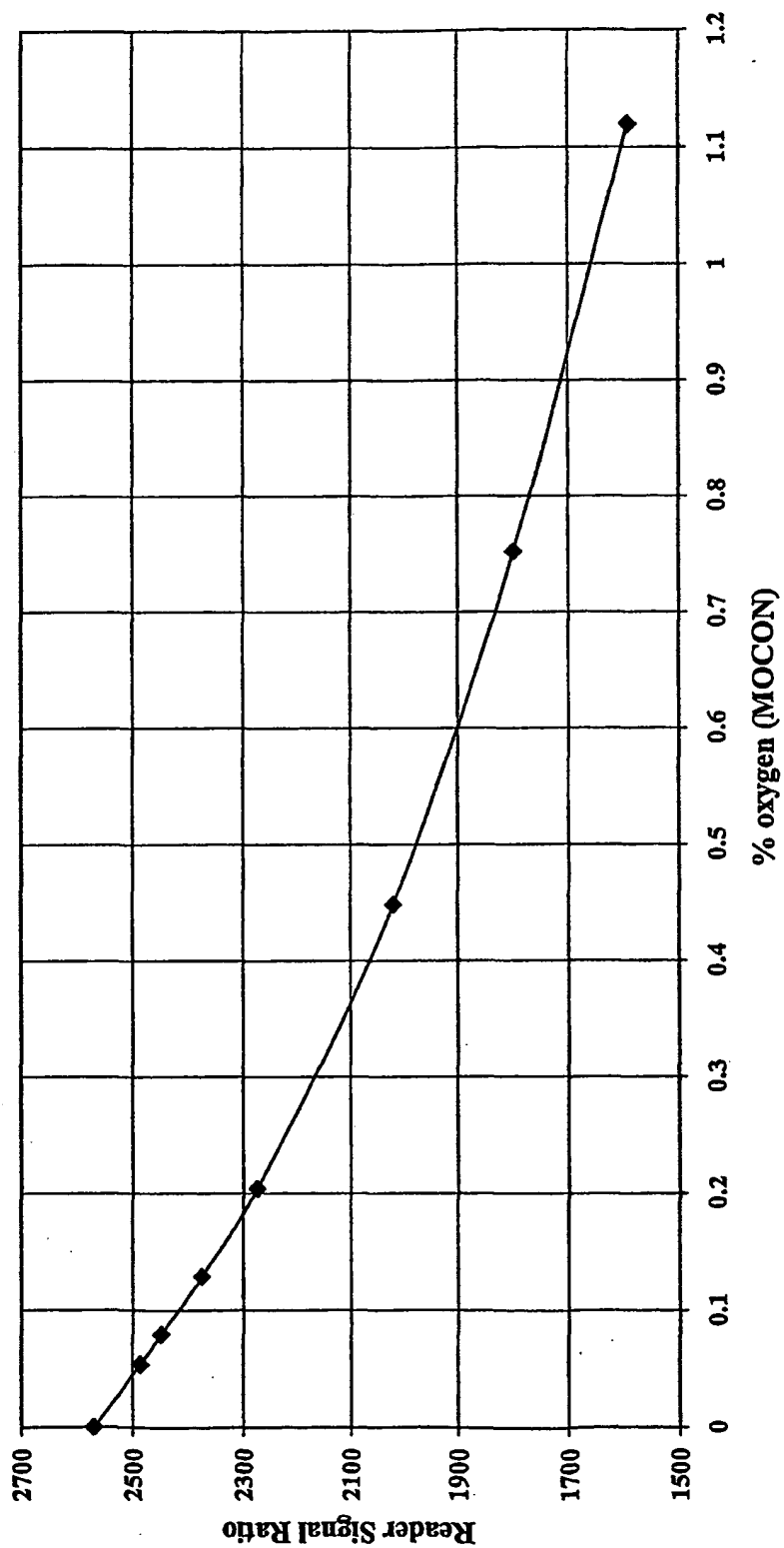


Figure 3

Emission spectra of PtOEP indicator in a thermal melt preparation of a commercial LDPE thermoplastic polymer. Excitation centered at 400nm.

**Emission Spectrum
PtOEP-LDPE**

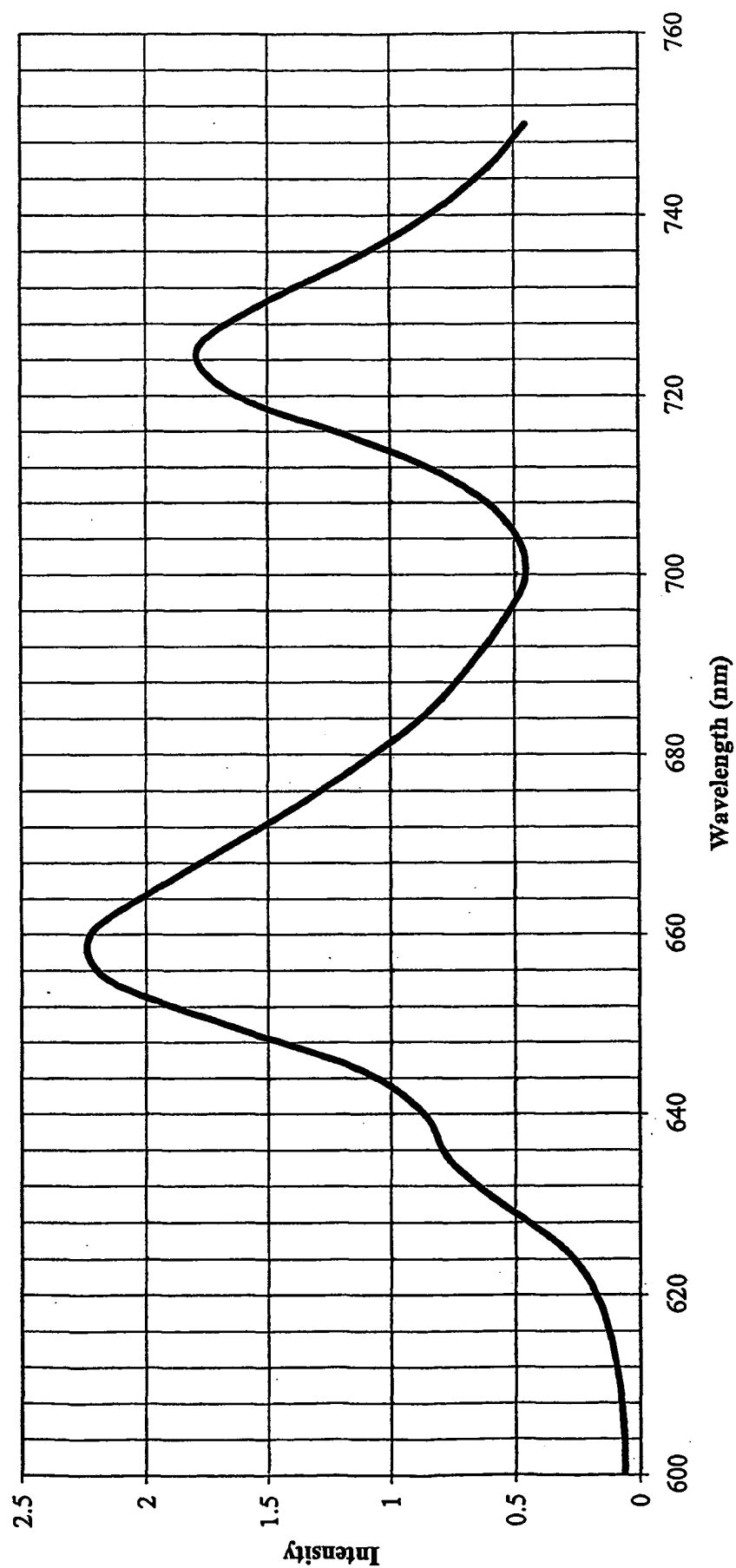


Figure 4
Ratiometric Response Curves for Press-Plaques from Different Carrier Polymers
Ratio Response of PdTRPP Indicator in Different Commercial Carrier Polymers

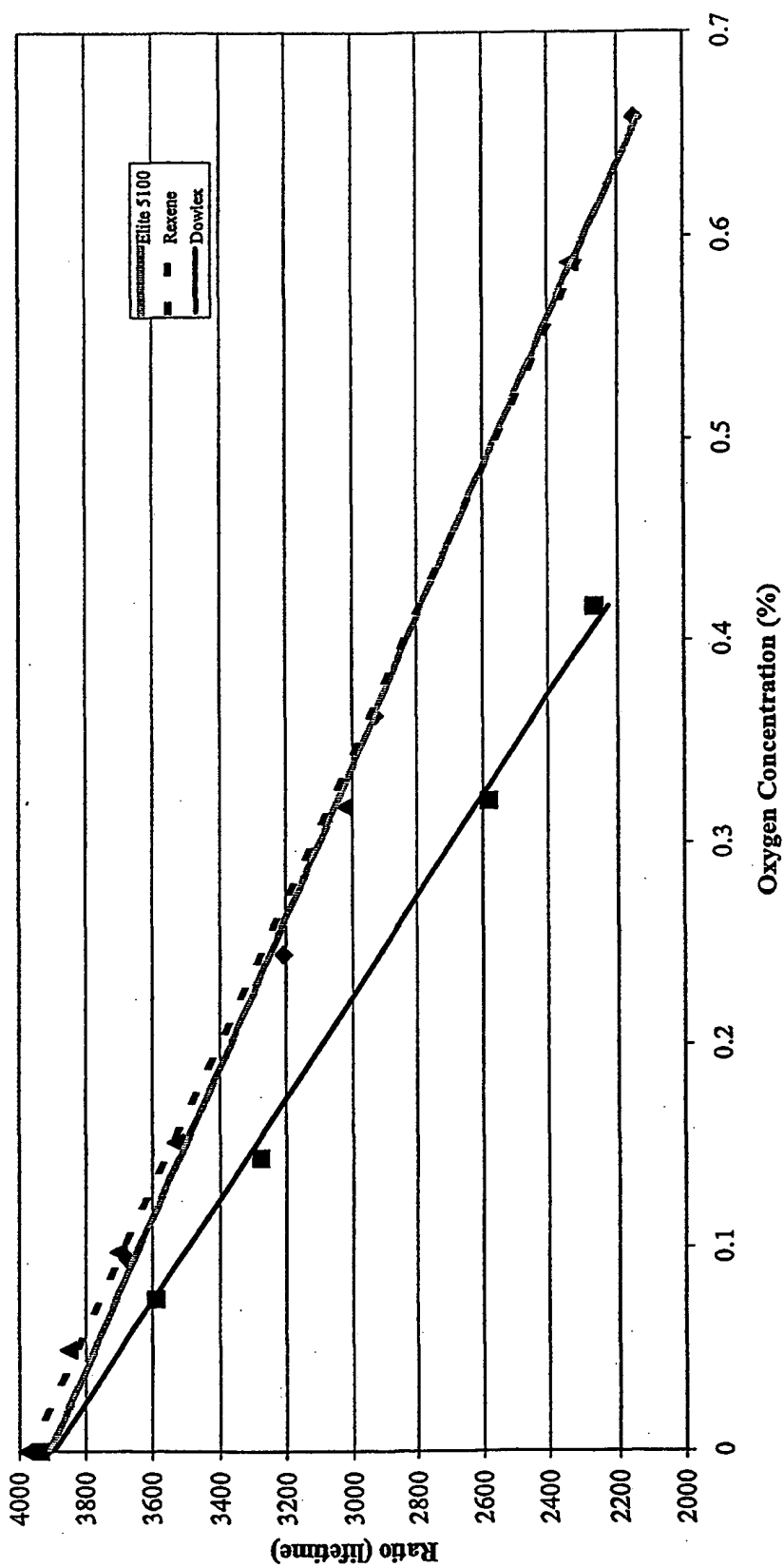


Figure 5
Ratio response of a PtOEP film prepared by extrusion in twin-screw extrusion machine

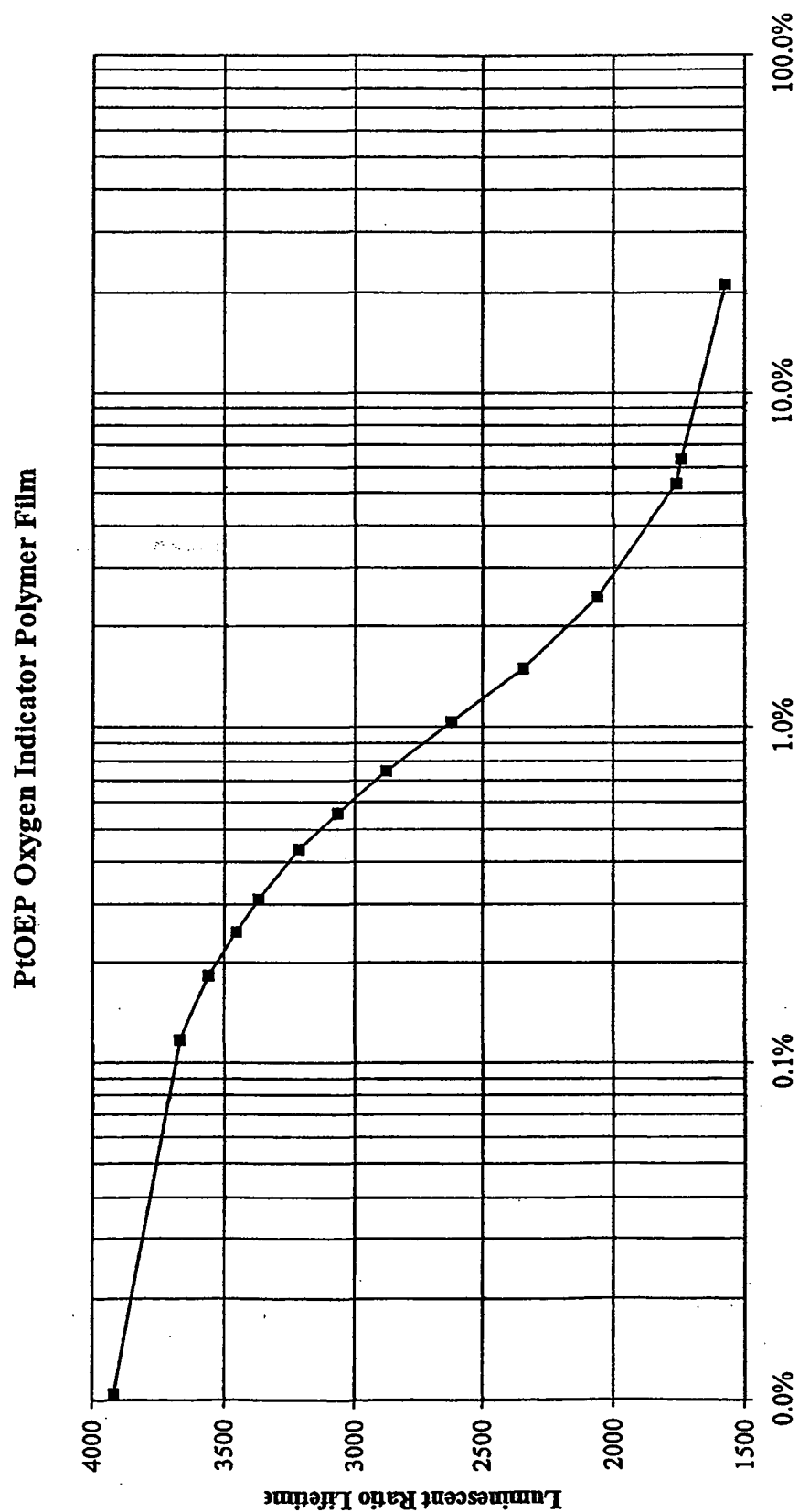
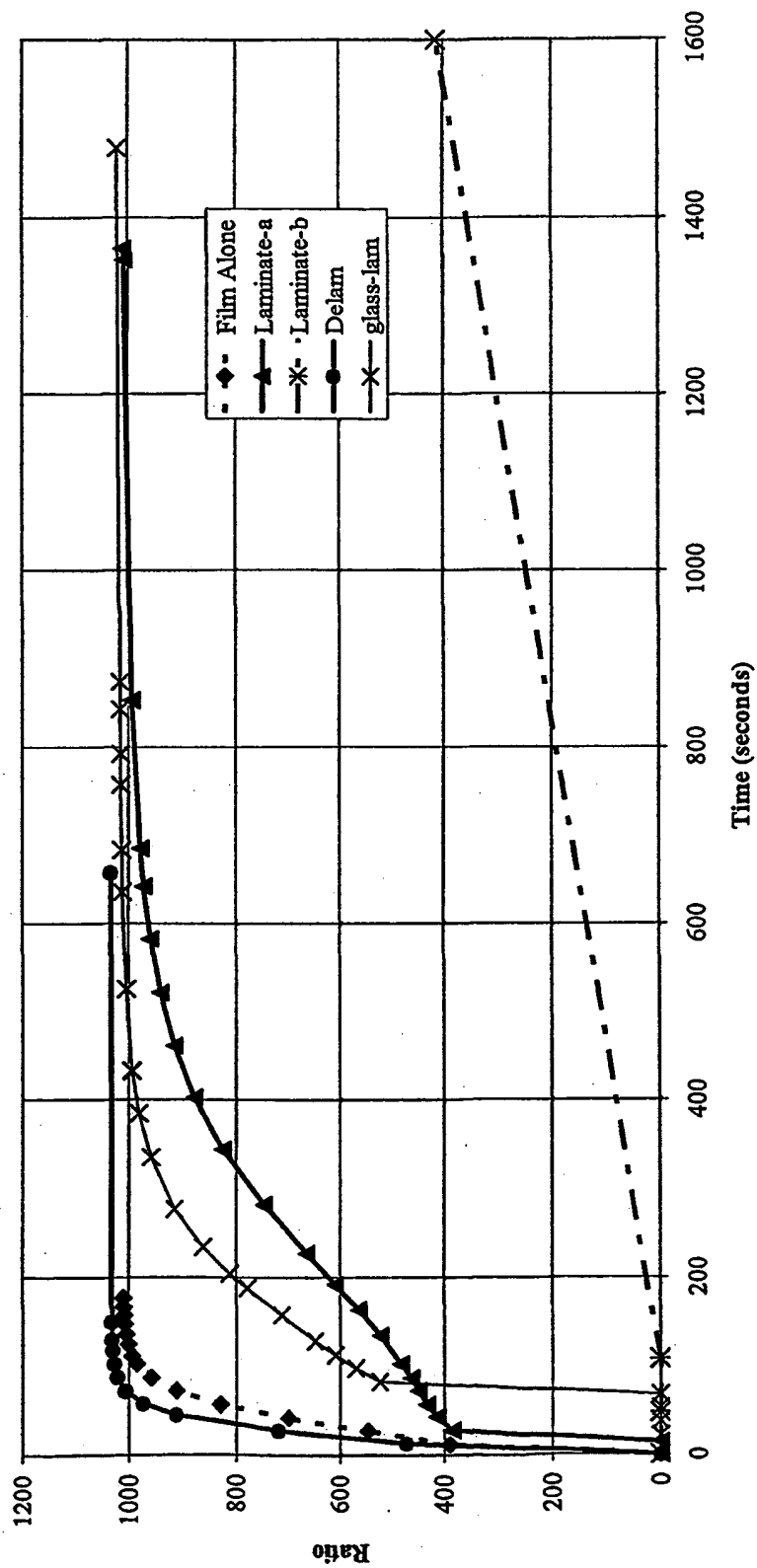


Figure 6

Various Laminate Forms of the Oxygen Sensor in Flexible Package Wrap Material

Indicator-Polymer Laminate Test Series
PtOEP/Dowlex Indicator Film



SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND
COMPOSITIONS PREPARED THEREBY

Technical Field

This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to macrocyclic polyester oligomer compositions and methods for modifying physical and chemical properties of the compositions. Even more particularly, this invention relates to macrocyclic polyester oligomer compositions having relatively low melting
5 temperatures.

Background Information

Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent
10 resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding. Linear polyesters may be produced from macrocyclic polyester oligomers.

15 Macrocyclic polyester oligomers (MPOs) have unique properties that make them attractive as matrices for engineering thermoplastic composites. These desirable properties stem from the fact that MPOs exhibit low melt viscosity, allowing them to impregnate a dense fibrous preform easily. Furthermore, certain MPOs melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate
20 catalyst, polymerization and crystallization can occur virtually isothermally. As a result, the time and expense required to thermally cycle a tool is favorably reduced.

Generally speaking, MPO compositions have high melting temperatures, which necessitate the use of special equipment in processing not commonly available in polymer processing units. If compositions with lower melting temperatures could be produced, it would
25 be possible to use more readily available processing equipment such as that is commonly used in the production and handling of epoxy resins.

→ 1a

EP-A-601753 discloses that the crystallinity of polyesters prepared from macrocyclic poly(1,4-butylene terephthalate) oligomers is reduced and cracking of molded parts suppressed by the incorporation therein of at least one other linear or macrocyclic poly(alkylene dicarboxylate) oligomer, such as poly(ethylene terephthalate) or poly(1,4-butylene isophthalate).

US-A-5191013 discloses thermoplastic polyester composites prepared from compositions comprising a filler, at least one macrocyclic poly(alkylene dicarboxylate) oligomer and a polymerization catalyst therefor.

US-A-5446122 discloses a method for making macrocyclic polyesters comprises the steps of supplying heat and contacting bis-hydroxy-alkyl-terminated diesters or oligomers thereof with high boiling point solvents and esterification catalysts.

EP-A-594385 discloses that macrocyclic poly(alkylene dicarboxylate) oligomers may be prepared in high yield by the reaction of a dicarboxylic acid chloride such as terephthaloyl chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate, in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine, in a substantially inert organic solvent such as methylene, chlorobenzene or a mixture thereof.

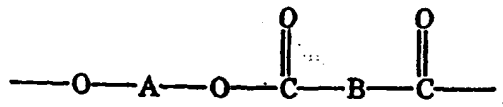
SUMMARY OF THE INVENTION

Physical and/or chemical properties of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, the presence of a single MPO species, the macrocyclic polyester tetramer, has an unexpectedly pronounced effect on the melting temperature of a MPO composition. Removal of a portion of the macrocyclic polyester tetramer can result in low-melting MPO compositions. The resulting MPO compositions have the further advantage, under many circumstances, of a greatly reduced tendency to crystallize at ambient temperatures, making it possible to combine them with fillers such as carbon or glass fibers to produce prepreps easily convertible to filled high molecular weight linear polyesters.

In one aspect, the invention is related to a process for modifying a physical property of a composition that includes MPOs.

According to one aspect of the present invention there is provided a process for modifying a physical property of a composition comprising macrocyclic polyester oligomers having different degrees of polymerization, comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural repeat unit of the formula



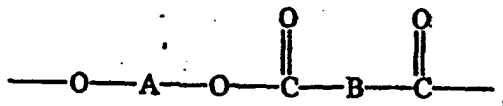
wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group and

B is a divalent aromatic or alicyclic group; and

(b) changing the weight percentage of at least one species of said macrocyclic polyester oligomers in said composition.

In another aspect, the invention provides a macrocyclic polyester oligomer composition comprising at least two species of macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group and

B is a divalent aromatic or alicyclic group;

wherein a species of said macrocyclic polyester oligomers having the highest melting temperature is present in an amount less than or equal to 5%.

→ 2a

In one embodiment, a blend material includes such a MPO composition and also a polymerization catalyst.

In a preferred embodiment, a MPO composition of the invention comprises 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers.

The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following figures, description, and claims.

Brief Description of Figures

The drawings are not necessarily to scale, emphasis instead being generally placed upon illustrating the principles of the invention to facilitate its understanding.

FIG. 1 is a schematic illustration of an embodiment of the invention including a fractional crystallization process.

Detailed Description

Physical properties, for example, the melting temperatures, of a composition comprising MPOs may be modified by modifying the weight percentage of a MPO species, for example, the macrocyclic polyester tetramer. A MPO composition having a low melting temperature can be

polymerized and processed at lower temperature thereby avoiding the need for special equipment not commonly available in polymer processing.

Definitions

The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

As used herein, "macrocyclic" means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

As used herein, a "macrocyclic polyester oligomer (MPO)" means a macrocyclic oligomer containing structural repeat units having an ester functionality. A MPO typically refers to multiple molecules of one specific formula. However, a MPO also may include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. In addition, a MPO may be a macrocyclic co-polyester oligomer (including macrocyclic multi-polyester oligomer), i.e., an oligomer having two or more different structural repeat units having an ester functionality within one cyclic molecule.

As used herein, "degree of polymerization (DP)" means the number of identifiable structural repeat units in oligomeric or polymeric backbone. The structural repeat units may have the same or different molecular structural. For example, "macrocyclic polyester tetramer" or "tetramer" refers to MPOs with a DP of 4.

As used herein, a "species" means MPOs having the same DP. For example, the macrocyclic polyester tetramer is one species.

As used herein, a "macrocyclic polyester oligomer composition" means a composition comprising a mixture of MPOs having different DP values, whether or not units of more than one molecular structure are present.

As used herein, a "blend material" means a mixture of two or more components including at least one MPO and at least one polymerization catalyst. Preferably the blend material is uniformly mixed. A blend material may also include a filler as well as other components recognized by a skilled artisan.

As used herein, "substantially homo- or co-polyester oligomer" means a polyester oligomer wherein the structural repeat units are substantially identical or substantially two different structural repeat units, respectively.

As used herein, "an alkylene group" means $-C_nH_{2n}-$, where $n \geq 2$.

As used herein, "a cycloalkylene group" means a cyclic alkylene group, $-C_nH_{2n-x}-$, where x represents the number of H's replaced by cyclization(s).

As used herein, "a mono- or polyoxyalkylene group" means $[-(CH_2)_m-O-]_n-(CH_2)_m-$, wherein m is an integer greater than 1 and n is an integer greater than 0.

5 As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure within.

10 As used herein, "a filler" means a material other than a MPO or a polymerization catalyst that may be included in the blend material. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester
15 polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silica, carbon black, titanium dioxide, organo bromides in combination with antimony oxides, calcium carbonate,
20 chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers.

As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as, a fibrous or particulate material. Illustrative examples of particulate materials are chopped fibers, glass microspheres, and crushed stone.

25 As used herein, "an equilibrated mixture" means a mixture of MPOs in thermodynamic or kinetic equilibration.

As used herein, "fiber" means any material with elongated structure such as polymer or natural fibers. The material can be fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

30 As used herein, a "tow" or "strand" means a group of fibers together, or a bundle of fibers, which are usually wound onto spools and may or may not be twisted. These tows or strands can be woven or knitted to form fabrics.

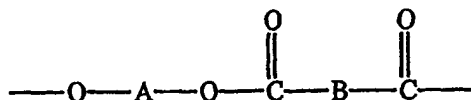
As used herein, a "fiber preform" means an assembly of fiber tows and/or fabric held together in a desired shape. Typically, fiber preforms are dry, and often held together with various tackifiers.

As used herein, a "prepreg" means a fiber material such as carbon fiber, glass fiber, or other fiber, that has been impregnated with a resin material in sufficient volume as to provide the matrix of the composite, and such that the ratio of fiber to resin is closely controlled. The fiber configuration can be in tow form, woven or knitted into a fabric, or in a unidirectional tape.

I. Macrocyclic Polyester Oligomers (MPOs)

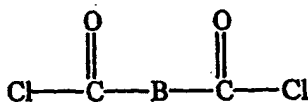
Many different MPOs can readily be made and are useful in the practice of this invention.

MPOs that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group. MPOs that may be employed in this invention may have various DP values, e.g., 2 to 20, 2 to 10, 2 to 8, and 2 to 6.

MPOs may be prepared by known methods. Synthesis of the preferred MPOs may include the step of contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such an amine is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

MPOs have also been prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate. The condensation typically occurs in the presence of a highly unhindered amine or a mixture thereof with at least one other

tertiary amine such as triethylamine. Usually, a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof is used. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

Another method for preparing MPOs, including macrocyclic co-polyester oligomers, is to
5 depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to MPOs by heating a mixture of linear polyesters, an organic solvent, and a trans-esterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et*
10 *al.*

It is also within the scope of the invention to employ macrocyclic homo- and co-polyester oligomers to produce homo- and co-polyester polymers, respectively. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to a MPO may also include co-polyester embodiments.

Among homopolymeric compositions and in one embodiment, MPOs of poly(1,4-
15 butylene) terephthalate (PBT) are used. Among homopolymeric compositions and in another embodiment, MPOs of polyethylene terephthalate (PET) are used. Among co-polymeric compositions and in one embodiment, MPO species contain a major proportion of PBT structural units, PET structural units, or both. In one embodiment, MPO species contain at least about 90
20 mole percent of PBT structural units, PET structural units, or both. In another embodiment, MPO species contain predominately PBT, and a minor proportion of other units, for example, poly(alkylene dicarboxylate) units or ether oxygen-containing units such as those in which A is derived from diethylene glycol.

II. Designing Physical and Chemical Properties of MPO Compositions

25 In one embodiment, MPO compositions are created that have physical and/or chemical properties different from that of the unmodified MPO compositions originally produced. For example, the melting temperatures of a MPO composition can be significantly decreased by removal from the MPO composition of a major proportion of the macrocyclic polyester tetramer, i.e., the oligomer having a DP of 4. This is possible because the tetramer is both high melting
30 and highly crystalline among the MPOs. Therefore, removal has a significant effect on the melting temperature and crystallinity of the oligomer composition. Similarly, the melting temperatures of a MPO composition can be significantly increased by adding into the MPO composition a significant proportion of the macrocyclic polyester tetramer.

preparation. In another embodiment, the weight percentage reduction is 70%. In yet another embodiment, the weight percentage reduction is 90%.

Any processes that result in modification of the weight percentage of a species of the MPOs may be employed. The effectiveness of such processes may be dependent on factors including the nature of the original MPO composition and the particular species the proportion of which is to be modified. Illustrative examples of such processes include distillation, fractional crystallization, anti-solvent precipitation, addition and mixing, chemical reactions, etc.

In one embodiment, removal of a species of MPOs is achieved by fractional crystallization. In one embodiment, the macrocyclic polyester tetramer is removed by fractional crystallization from a solution of the MPO composition. Any solvent that facilitates fractional crystallization may be employed. Illustrative suitable solvents include aromatic hydrocarbons and halogenated aromatic hydrocarbons, such as toluene, xylene and *o*-dichlorobenzene (ODCB). For example, in one embodiment, a 5% by weight solution of oligomer composition in ODCB at 110°C is cooled to ambient temperature of about 25°C, whereupon a precipitate forms that contains a major proportion of the tetramer.

In one embodiment, removal of the macrocyclic polyester tetramer is achieved by anti-solvent precipitation. Illustrative suitable non-solvents include aliphatic hydrocarbons, especially those in the C₆₋₁₀ range such as hexane, heptane, octane and decane. In one preferred embodiment, heptane is used.

In one embodiment of a process of removing macrocyclic polyester tetramer by anti-solvent precipitation, the non-solvent is added to the MPO solution at an elevated temperature, in the range of about 80-120°C, after which the mixture is allowed to cool to a lower temperature, typically no higher than about 70°C since at lower temperatures substantial amounts of other oligomers, or the MPO composition in its entirety, may be precipitated. The amount of non-solvent added is most often about 90-110% by volume of solvent used. Upon cooling to this lower temperature, a precipitate forms that is predominantly the macrocyclic polyester tetramer. A minor proportion of the macrocyclic polyester tetramer originally present usually remains in the MPO composition in solution. However, the remaining macrocyclic polyester tetramer does not have a significant effect on the melting temperature and crystallinity of the MPO composition.

The MPO species removed may be reused for various purposes. In one embodiment, the MPO species, e.g., macrocyclic polyester tetramer, is polymerized separately or in combination with other MPOs or linears to produce linear polyester. In another embodiment, the MPO

In one aspect, the invention relates to a process for modifying a physical property of a composition having MPOs. The method includes the steps of (a) providing a composition having at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. It should be understood that compositions may have three, four, 5 or five or more species of MPOs present. In addition, although preferably the weight percentage of one species of the MPOs in the composition is changed, the invention contemplates changing more than one species in a composition.

In one embodiment, the physical property to be modified is the melting temperature of the composition. Besides melting temperature, other physical properties that may be modified by the 10 method of the invention include, for example, crystallinity and viscosity. Modification of a selected physical property may be achieved by either increasing or reducing the weight percentage of at least one species of the MPOs in the composition.

In one embodiment, the weight percentage of at least the species having the highest melting temperature is reduced in step (b). In one embodiment, the weight percentage of at least 15 macrocyclic polyester tetramer is reduced in step (b). In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, a MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

20 The proportion of macrocyclic polyester tetramer present in products prepared by reactions under thermodynamic control is generally greater than the proportion resulting from reactions under kinetic control. An example of a thermodynamically controlled reaction is depolymerization. The reaction of a diol with a dicarboxylic acid chloride is chiefly kinetically controlled.

25 In one embodiment, the proportion of macrocyclic polyester tetramer removed according to the invention is at least 60% by weight of the total amount of the macrocyclic polyester tetramer in the oligomer composition as originally prepared. The amount of macrocyclic polyester tetramer present can vary according to the method of preparation of the oligomer composition. In another embodiment, at least 70% of the macrocyclic polyester tetramer is 30 removed. In yet another embodiment, at least 90% removal is performed.

In one embodiment, the reduction of the weight percentage of the macrocyclic polyester tetramer results in its weight percentage in the modified composition to be 60% less than its weight percentage in an equilibrated mixture of the MPOs according to the method of

species is equilibrated with linear polyester that is intended to be depolymerized, either before or during the depolymerization reaction. Depolymerization of a mixture of linear polyester and the MPO species removed from a MPO composition provides an oligomeric product that has the same distribution of oligomers as that obtained from linear polyester alone, showing that

5 equilibration is essentially complete.

The apparatus for performing the above modification processes may be any conventional apparatus. The actual apparatus will depend on the actual process being employed. In one embodiment for performing fractional crystallization (referring to FIG. 1), an apparatus for producing the compositions of the invention may include a reactor vessel 110 in which the

10 reaction constituents 120, e.g., linear polyester, solvent and depolymerization catalyst, are combined and the depolymerization reaction conducted. Subsequently, the product mixture passes through a filter 130 to remove linears. The filtrate may pass into a second vessel 140 where it is cooled to room temperature either in the presence or absence of aliphatic hydrocarbon as non-solvent to precipitate a species of MPO, e.g., the tetrameric species. The filtrate is then

15 passed through another filter 150 which removes the precipitate, e.g., macrocyclic polyester tetramer. The precipitated macrocyclic polyester oligomers can be removed from the filter 150 and recycled to the reactor vessel 110. Further vessels may be employed downstream to isolate the product in the desired form and to remove non-solvent when it is employed.

In a preferred embodiment of the invention, a MPO composition includes at least two

20 species of MPOs wherein the species having the highest melting temperature is present in an amount less than or equal to 10%, preferably less than or equal to 5%, more preferably less than or equal to 3%.

In one embodiment, the MPOs in the MPO composition have a DP from 2 to about 20. In another embodiment, the MPOs have a DP from 2 to about 10. In another embodiment, the

25 MPOs have a DP from 2 to about 8. In yet another embodiment, the MPOs have a DP from 2 to about 6.

In one embodiment, the species having the highest melting temperature is macrocyclic polyester tetramer. In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers.

30 The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, the MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

In one embodiment, the MPO composition includes 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers. In some embodiments, the percentage of macrocyclic polyester tetramers preferably is less than about 3%, more preferably less than about 2%, or most

5 preferably less than about 1%.

In one embodiment, the MPO composition includes a filler. In another embodiment, the MPO composition includes a polymerization catalyst. In another embodiment, the MPO composition is part of a prepreg composition.

MPO compositions in which a major proportion of the macrocyclic polyester tetramer has
10 been removed have melting temperatures significantly lower than those of corresponding compositions containing macrocyclic polyester tetramer in the original proportions, i.e., the unmodified product mixtures (equilibrated or nearly equilibrated) of the MPO-forming reactions. The melting temperatures typically are wide ranges by reason of the various kinds of MPO molecules in the MPO compositions. The most pronounced decrease in temperature is in the
15 upper value of the range, i.e., the temperature at which the last trace of solid melts. Typically, the upper value of the melting temperature range of a modified MPO composition may be from about 15°C to as much as 70°C lower than the upper value for the unmodified original MPO composition.

This decrease in melting temperature is typically accompanied by a significant decrease in
20 crystallinity, particularly upon heating above the melting temperature followed by quenching. Thus, MPO compositions in which macrocyclic polyester tetramer has been removed can be quenched and used to impregnate fibrous or other fillers, whereupon a prepreg composition capable of being draped and shaped is produced.

III. Polymerization catalysts

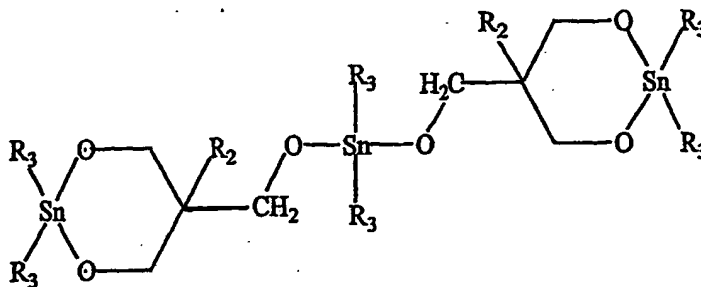
25 Polymerization catalysts that may be employed in the invention are capable of catalyzing the polymerization of MPOs. Organotin and organotitanate compounds are preferred catalysts, although other catalysts may be used. For example, organotin compound 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane may be used as polymerization catalyst. Other illustrative organotin compounds include n-butyltin(IV) chloride dihydroxide, dialkyltin(IV)
30 oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and

trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.*

Also, trisstannoxanes having the general formula (I) shown below can be used as a polymerization catalyst to produce branched polyester polymers.

5

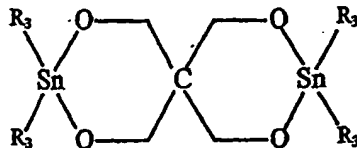
(I)



where R_2 is a C_{1-4} primary alkyl group and R_3 is C_{1-10} alkyl group.

10 Additionally, organotin compounds with the general formula (II) shown below can be used as a polymerization catalyst to prepare branched polyester polymers from MPOs.

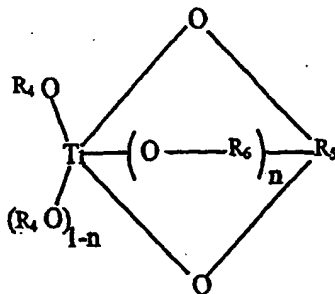
(II)



15 where R_3 is defined as above.

As for titanate compounds, tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds with the general formula (III) shown below can be used as polymerization catalysts.

(III)



20

wherein: each R_4 is independently an alkyl group, or the two R_4 groups taken together form a divalent aliphatic hydrocarbon group; R_5 is a C_{2-10} divalent or trivalent aliphatic hydrocarbon group; R_6 is a methylene or ethylene group; and n is 0 or 1.

Typical examples of titanate compounds with the above general formula are shown in

5 Table 1.

Table 1. Examples of Titanate Compounds Having Formula (III)

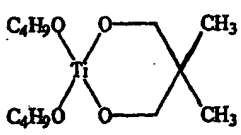
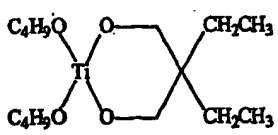
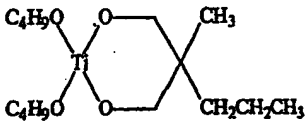
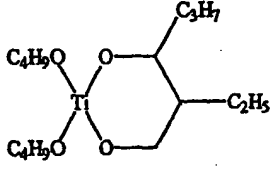
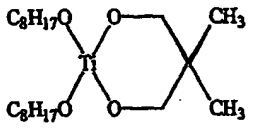
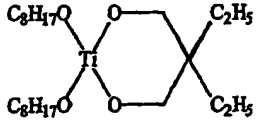
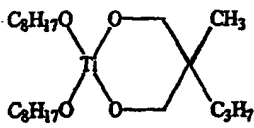
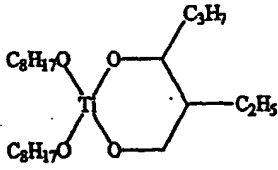
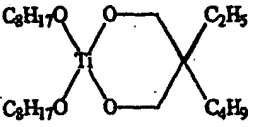
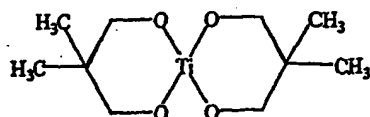
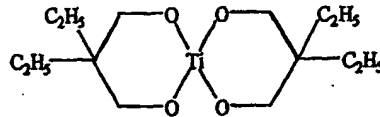
 <p>Di-1-butyl 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di-1-butyl 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-butyl)-2-ethylpropane-1,3-dioxytitanate</p>	

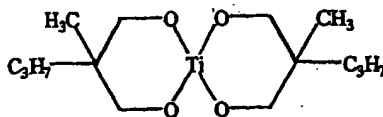
Table 1. Examples of Titanate Compounds Having Formula (III) (Cont'd)



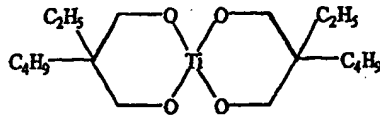
Bis(2,2-dimethyl-1,3-propylene) titanate



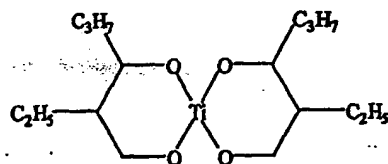
Bis(2,2-diethyl-1,3-propylene) titanate



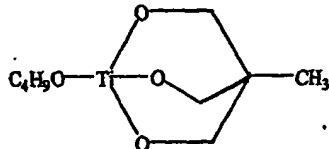
Bis(2-(1-propyl)-2-methyl-1,3-propylene) titanate



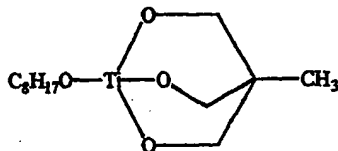
Bis(2-(1-butyl)-2-ethyl-1,3-propylene) titanate



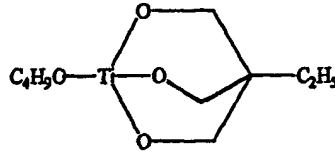
Bis(2-ethyl-1,3-hexylene) titanate



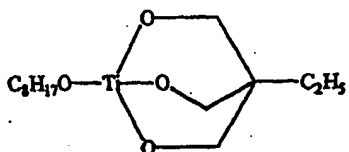
1-(1-Butoxy)-4-methyl-2,6,7-trioxo-1-titanabicyclo[2,2,2]octane



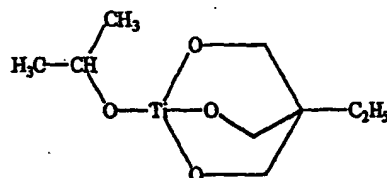
1-(2-ethyl-1-hexoxy)-4-methyl-2,6,7-trioxo-1-titanabicyclo[2,2,2]octane



1-(1-Butoxy)-4-ethyl-2,6,7-trioxo-1-titanabicyclo[2,2,2]octane



1-(2-ethyl-1-hexoxy)-4-ethyl-2,6,7-trioxo-1-titanabicyclo[2,2,2]octane

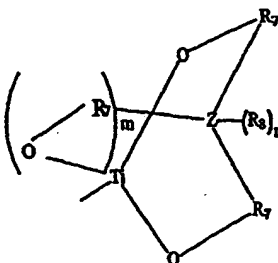


1-(2-Propoxy)-4-ethyl-2,6,7-trioxo-1-titanabicyclo[2,2,2]octane

5

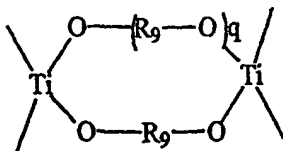
Titanate ester compounds having at least one moiety of the following general formula have also been used as polymerization catalysts:

(IV)



or

(V)



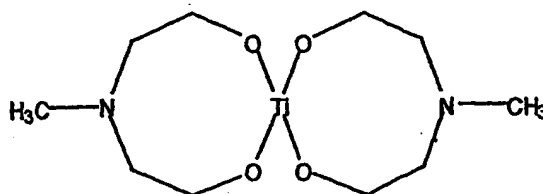
wherein:

each R_7 is independently a C_{2-3} alkylene group;5 R_8 is a C_{1-6} alkyl group or unsubstituted or substituted phenyl group; Z is O or N; provided when Z is O, $m = n = 0$, and when Z is N, $m = 0$ or 1 and $m + n = 1$;each R_9 is independently a C_{2-6} alkylene group; and q is 0 or 1.

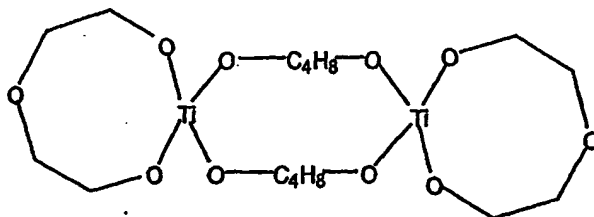
Typical examples of such titanate compounds are shown below as formula (VI) and formula (VII):

10

(VI)



(VII)



IV. The Blend Material

A blend material comprising MPOs and a polymerization catalyst allows for easy production, storage, transportation and processing. From the standpoint of applications, the blend material is a one-component ready-to-use mixture. The blend material may also be processed like a thermoset while producing a thermoplastic. Furthermore, the blend material may eliminate the need for existing equipment to be modified to allow for transfer of the MPO and a polymerization catalyst into the equipment in the appropriate amounts at the appropriate time and at the appropriate temperature.

In one aspect, the invention relates to a blend material comprising a MPO composition with a modified physical property (e.g., the melting temperature as described above) and a polymerization catalyst.

There is no limitation with respect to the physical form of the MPO when mixed with the polymerization catalyst as long as the MPO remains substantially chemically intact. In one embodiment, the MPO is a solid such as a powder. In this embodiment, mechanical mixing typically is used to mix MPO with a polymerization catalyst. In another embodiment, the MPO is mixed in the presence of a solvent with the solvent remaining present during the step of mixing.

In one embodiment, the blend material also includes a filler as described above. Illustrative examples of such fillers include pigments, light weight fillers, flame retardants, and ultraviolet light stabilizers. For example, calcium carbonate may be used to increase the thickness of a polyester polymer product to improve its mechanical performance. Also, glass microspheres may be added to lower the density of the product. Other fillers include nanoclays, e.g., to increase the modulus of the product, organo bromides in combination with antimony oxides, e.g., to impart flame resistance, and colorants such as carbon black or titanium dioxide.

The filler is added generally between about 0.1% and 70% by weight, between about 25% and 70% by weight, or between about 2% and 5% by weight depending on the filler and the purpose for adding the filler. For example, the percentage is preferably between 25% and 50% by weight in the case of calcium carbonate, between 2% and 5% by weight in the case of nanoclays, between 0.1% and 1% in the case of pigments, and between 25% and 70% by weight in the case of glass microspheres.

A process for preparing the blend material includes providing a MPO and mixing the MPO with a polymerization catalyst. When preparing the blend, the MPO and the polymerization catalyst may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the MPO with the polymerization catalyst via agitation at temperatures below the melting temperature of the MPO. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

A solvent may also be employed to assist in the uniform mixing of the MPO with the polymerization catalyst. Various solvents can be used, and there is no limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water. Illustrative examples of solvents that may be employed in the invention include methanol,

ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

There is no limitation with respect to the amount of solvent to be employed other than that the amount results in a uniform mixing of the MPO and the polymerization catalyst. In one embodiment, the blend of MPO with the polymerization catalyst is isolated either by direct removal of the solvent via evaporation or by precipitation via addition of the mixture into a nonsolvent. In another embodiment, the blend of solid ingredients is further dried under vacuum at elevated temperatures below the melting temperature of the MPO to remove any residual solvent.

A process for preparing the blend material further having at least one filler, or any other additional material, is generally the same as described above, however, the characteristics of the filler and/or additional materials must be considered. It should be understood that the MPO, the polymerization catalyst, the filler, any additional material(s) and/or solvent, if used, may be mixed in any order or simultaneously as long as the final composition contains the appropriate amount of each ingredient.

It is within the scope of the invention to employ one, two or more different fillers in preparing a blend material of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to filler in singular also includes an embodiment wherein two or more different fillers are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to fillers in plural also includes an embodiment wherein one filler is employed.

In one embodiment of the invention, the amount of polymerization catalyst employed is generally about 0.01 to about 10.0 mole percent, preferably about 0.1 to about 2 mole percent, and more preferably about 0.2 to about 0.6 mole percent based on total moles of monomer repeat units of the MPO.

Although dependent on the particular composition of the blend material, blend materials typically exhibit a shelf life generally longer than a week, and preferably longer than a month, and more preferably longer than a year when stored at ambient temperature.

It is within the scope of the invention to employ one, two or more different polymerization catalysts in preparing a blend of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in singular also includes an embodiment wherein two or more different polymerization catalysts are employed. Similarly, unless stated otherwise, any embodiment of a

composition, article or process that refers to polymerization catalyst in plural also includes an embodiment wherein one polymerization catalyst is employed. Two or more polymerization catalysts may be used to vary the rate of polymerization and to produce polyesters with variable degrees of branching.

5 **V. Polymerization of MPOs**

In another aspect, the invention relates to a process for polymerizing a MPO composition that includes the steps of (a) providing a MPO composition with a modified physical property (e.g., the melting temperature as described above), (b) providing a polymerization catalyst, and (c) polymerizing the MPOs. The MPOs and the polymerization catalyst may be components of a
10 blend material. Therefore, in one embodiment, a process for polymerizing a MPO composition includes the steps of (a) providing a blend material having a MPO composition with a modified physical property, e.g., the melting temperature, and (b) polymerizing the MPOs. In one embodiment, the polymerization is conducted in the range of 130 °C to 230 °C.

By reason of the lower melting temperature and decrease in crystallinity, it is frequently
15 possible to polymerize the compositions of the present invention to linear polyesters at lower temperatures than with previously known MPO compositions. For example, a conventionally prepared macrocyclic PBT oligomer composition may require a polymerization temperature (in the presence of a conventional tin compound as catalyst) on the order of 190°C and will not polymerize at 150°C. The corresponding composition, from which most of the tetramer has been
20 removed according to this invention, has been polymerized to high molecular weight PBT at temperatures as low as 148°C.

In other respects, the compositions of MPOs in which tetramers have been removed are similar to known MPO compositions in that they may be polymerized under a wide variety of conditions in the presence of polymerization catalysts to linear polyesters having a wide variety
25 of uses.

Blends of MPOs with catalyst and/or filler may be polymerized in processes such as rotational molding, resin film infusion, pultrusion, resin transfer molding, filament winding, making and using powder-coated or hot melt prepreg, water slurry process, compression molding, and roll wrapping. These processes may be used to form polyester compositions,
30 including composites, which may be included in articles of manufacture such as carbon fiber golf shafts and lightweight automotive chassis members, construction materials, and so on.

The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention.

Example A General Depolymerization Procedure

- 5 Dissolve dry poly(1,4-butylene terephthalate) (PBT) pellets in dry o-dichlorobenzene (ODCB) under inert atmosphere at 180°C. Add a titanate catalyst as a solution in ODCB or as a neat solid. The depolymerization reaction is carried out at about 180°C. The reaction can be sampled over time to determine progress. When equilibrium is reached (usually within 1 hour), the reaction is cooled to 100°C and water is added to quench the titanate catalyst
10 (add about 0.5% water by volume). After quenching, the reaction mixture is concentrated by removing 70-95% of the ODCB. This step can be done from 70-180°C by adjusting pressure during the strip.

- After the initial concentration step, the reaction is allowed to cool to about 70°C and filtered to remove the bulk of the linears which fall from solution. The filtrate, which contains
15 the MPOs, is concentrated to about 30% solids at about 110°C. An equal volume of heptane is added and the reaction is allowed to cool to about 70°C to precipitate the PBT tetramer. Filter to remove the PBT tetramer and pass the filtrate through a column of alumina to remove residual linears. Pure MPOs are then isolated by heptane precipitation or by concentration.

- PBT used in these experiments was produced by General Electric (Valox 315 grade) and
20 was dried in *vacuo* at about 120°C before use. Anhydrous ODCB was used as received from Aldrich. Titanate catalysts were prepared from tetraisopropyl titanate from DuPont that was vacuum distilled prior to use. Diols that were dried over molecular sieves. All other reagent grade solvents and chemicals were used as received.

- HPLC analysis was used to characterize the composition of the MPOs and to follow
25 progression of depolymerization reactions. HPLC analysis was conducted using a Hewlett Packard Series 1050 chromatography system. Samples were eluted at 1.5 ml/min through a 4.6 x 15 cm Zorbax Eclipse XBD-C8 column at 40°C. A linear acetonitrile:water gradient which ramped from 50:05 to 100:0 over 18 min was used. Analysis was calibrated using pure PBT dimer which was isolated by vacuum sublimation. MPOs were quantified using phenanthrene as
30 an internal calibration standard. Peaks were measured at 254 nm with a UV detector.

Analyses for polymer M_w were conducted using a Hewlett Packard Series 1100 chromatography system. Samples were eluted at 1 ml/min with chloroform through a bank of

two Phenomenex Phenogel 5 μ m linear 300 x 7.8 mm columns at 40°C. Peaks were detected with a UV detector at 254 nm and the instrument was calibrated using polystyrene standards.

HPLC retention times of MPOs are shown in Table 1. Melting range data of select MPO compositions is shown in Table 2.

5

Table 1. HPLC Retention Times of Select MPOs

MPO	Dimer (PBT)	Trimer (PBT)	Tetramer (PBT)	Pentamer (PBT)
HPLC T _r (min.)	6.8	11.5	13.6	15.4

Table 2. Melting Ranges of Select MPO Compositions

Sample	%Dimer	%Trimer	%Tetramer	%Pentamer	% co-MPO	Melt Range °C
a	13.1	12.9	51.9	11.7	9.3	175-218
b	2	46.7	29.8	21.5	0	120-215
c	32.2	38.2	16.6	13.1	0	120-200
d	34.5	29.9	12.8	11.2	13.8	125-175
e	30.6	34.3	10.2	10.2	14.2	125-168
f	37.1	37	1.48	10	14.5	125-148

10 Example 1

A 22.2 g sample of commercially available PBT was dissolved in 1,450 g (1,107 ml) of ODCB and depolymerized in the presence of 2.8 mole percent of a mixed 1,4-butanediol/2-methyl-2,4-pentanediol (4.3:1 molar) titanate catalyst. MPOs were obtained in the amount of 11.4 g, or 51.8% of theoretical.

15 The reaction mixture was quenched with water at 100°C and ODCB was distilled off to a MPO concentration of 11% by weight (71 ml of ODCB). A sample was removed and stripped of solvent; it was found to have a melting temperature of 100-210°C.

Heptane, 71 ml, was added to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool to 70°C, whereupon a precipitate formed. The mixture was
20 filtered; the filtration residue was found by HPLC analysis to contain about 96% by weight of the tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-150°C.

Example 2

A 250 ml round-bottomed flask equipped with a magnetic stirrer was charged with 85 g
25 (64 ml) of ODCB and 15 g of a macrocyclic PBT oligomer composition prepared by the reaction

of terephthaloyl chloride with bis(4-hydroxybutyl) terephthalate. A control sample of the oligomer composition was found to have a melting temperature of 100-180°C.

Heptane, 64 ml, was added slowly to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool over 1 hour to 75°C, whereupon a precipitate formed.

- 5 The mixture was filtered; the filtration residue was found to contain about 90% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-130°C.

Example 3

- 10 A 3 l round-bottomed flask equipped with a magnetic stirrer and thermometer was charged with 700 g (534 ml) of ODCB and 300 g of a macrocyclic PBT oligomer composition prepared by the reaction of terephthaloyl chloride with 1,4-butanediol. A control sample of the oligomer composition was found to have a melting temperature of 120-175°C.

- 15 The mixture was heated to 110°C to dissolve all of the oligomers and heptane, 534 ml, was added slowly at 110°C. The reaction mixture was allowed to cool to 75°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found to contain about 73% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 120-158°C.

20 *Example 4*

- A 5% (by weight) solution in ODCB of macrocyclic PBT oligomers, prepared as described in Example 1, was found to be a homogeneous liquid at 110°C. Upon cooling to room temperature, a precipitate deposited from the solution. The precipitate was found by analysis to be 90% pure cyclic tetramer, and to constitute 60% by weight of the tetramer present in the
25 original oligomer composition.

Example 5

- A 300 mg control sample of the PBT oligomer composition employed in Example 2, from which the tetramer had not been removed, was placed in a test tube and submerged in an oil bath maintained at 150°C for 10 minutes. The composition did not melt at this temperature. A
30 sample of the product of Example 2, from which tetramer had been removed, melted when heated to the same temperature but crystallized to an opaque, brittle solid upon cooling.

When the product of Example 2 was heated to 150°C and quenched by submersion in cold water, it remained transparent, indicating that it was amorphous rather than crystalline after quenching. It remained amorphous and tacky after storing at ambient temperature for one month. By contrast, the control returned to a brittle, crystalline state upon standing for 48 hours.

5 *Example 6*

A 3 l round-bottomed flask was charged with 3,098 ml of ODCB, 26.3 g of commercially available PBT pellets, and 4.9 g of tetramer removed from a MPO composition as described in Example 3. The resulting mixture was heated to 180°C until all solids were dissolved and a titanate catalyst similar to that of Example 1 was added in a similar proportion to PBT. Heating
10 at 180°C was continued for one hour, after which a portion of the mixture was analyzed and found to contain MPOs in a proportion similar to that observed in Example 1.

While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions and examples should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one
15 skilled in the art without departing from the spirit and scope of the present invention.

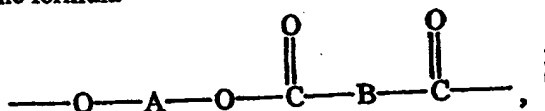
The patents and references referred to above are incorporated by reference including:
U.S. Patent Nos. 5,039,783, 5,191,013, 5,231,161, 5,348,985, 5,389,719, 5,407,984, 5,466,744,
5,591,800, 5,661,214, 5,668,186, and 5,710,086.

What is claimed is: _____

CLAIMS

1. A process for modifying a physical property of a composition comprising macrocyclic polyester oligomers having different degrees of polymerization, comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group

and

B is a divalent aromatic or alicyclic group; and

(b) changing the weight percentage of at least one species of said macrocyclic polyester oligomers in said composition.

2. A process as claimed in claim 1 wherein said physical property is the melting temperature of said composition.

3. A process as claimed in claim 1 or 2 wherein said at least one species of said macrocyclic polyester oligomers in step (b) is the highest melting temperature macrocyclic polyester oligomer in said composition.

4. A process as claimed in claim 1 or 2, wherein said at least one species of said macrocyclic polyester oligomers in step (b) comprises at least said macrocyclic polyester tetramer.

5. A process as claimed in claim 4, wherein step (b) comprises reducing the weight percentage of at least the macrocyclic polyester tetramer.

6. A process as claimed in any one of the preceding claims, wherein said at least two species of macrocyclic polyester oligomers in step (a) have a degree of polymerization from 2 to 10.

7. A process as claimed in claim 6, wherein said at least two species of macrocyclic polyester oligomers in step (a) have a degree of polymerization from

2 to 6.

8. A process as claimed in any one of the preceding claims, wherein said composition comprises macrocyclic poly(1,4-butylene terephthalate) oligomers.

9. A process as claimed in any one of claims 1 to 7 wherein said composition comprises macrocyclic poly(ethylene terephthalate) oligomers.

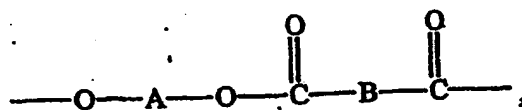
10. A process as claimed in any one of claims 1 to 7, wherein said composition comprises a macrocyclic copolyester oligomer.

11. A process as claimed in claim 10 wherein said composition comprises a macrocyclic copolyester oligomer containing at least about 90 mole percent poly(1,4-butylene terephthalate) structural units.

12. A process as claimed in any one of claims 1 to 4 or any claim when dependent thereon either directly or indirectly wherein step (b) comprises performing fractional crystallization.

13. A macrocyclic polyester oligomer composition having a decreased melting temperature produced by the process of any one of the preceding claims.

14. A macrocyclic polyester oligomer composition comprising at least two species of macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group
and

B is a divalent aromatic or alicyclic group;

wherein a species of said macrocyclic polyester oligomers having the highest melting temperature is present in an amount less than or equal to 5%.

15. A composition as claimed in claim 14, wherein each of said macrocyclic polyester oligomers has a degree of polymerization in the range from 2 to about 6.

16. A composition as claimed in claim 15 wherein said species having the highest melting temperature is macrocyclic polyester tetramer.

17. A composition as claimed in claim 14, 15 or 16, wherein said macrocyclic polyester oligomers comprise macrocyclic poly (1,4-butylene terephthalate) oligomers.

18. A composition as claimed in claim 14, 15, 16 or 17, wherein said macrocyclic polyester oligomers comprise a macrocyclic copolyester oligomer comprising at least about 90 mole percent poly (1,4-butylene terephthalate) structural units.

19. A composition as claimed in claim 14, 15 or 16, wherein said macrocyclic polyester oligomers comprise macrocyclic poly(ethylene terephthalate) oligomers.

20. A composition as claimed in any one of claims 14 to 19, further comprising a filler.

21. A composition as claimed in any one of claims 14 to 20, further comprising a polymerization catalyst.

22. A prepreg composition comprising the composition as claimed in any one of claims 14 to 21.

23. A blend material comprising:

(a) the macrocyclic polyester oligomer composition as claimed in any one of claims 14 to 21; and

(b) a polymerization catalyst.

24. A blend material as claimed in claim 23, further comprising a filler.

25. A blend material as claimed in claim 24, wherein said filler is present at a weight percentage of from 0.1% to 70%.

26. A polyester polymer composition prepared by polymerizing said macrocyclic polyester oligomers of said blend material of any one of claims 23 to 25.

27. An article of manufacture comprising said polyester polymer composition of claim 26.

28. A process for polymerizing a macrocyclic polyester oligomer composition comprising the steps of:

(a) providing the macrocyclic polyester oligomer composition as claimed in any one of claims 14 to 21;

(b) providing a polymerization catalyst; and

(c) polymerizing said macrocyclic polyester oligomers.

29. A process for polymerizing a macrocyclic polyester oligomer composition comprising the steps of:

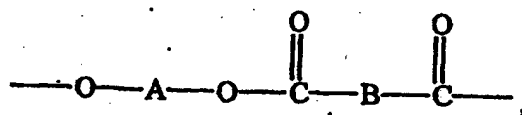
(a) providing the blend material as claimed in any one of claims 23 to 25;

and

(b) polymerizing said macrocyclic polyester oligomers.

30. A process as claimed in claim 29, wherein step (b) is conducted at a temperature between 130°C and 230°C.

31. A macrocyclic polyester oligomer composition comprising 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers, each of said macrocyclic macrocyclic polyester oligomers comprising a structure repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,

and

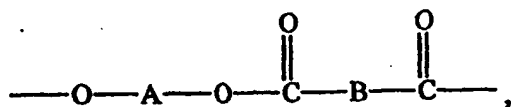
B is a divalent aromatic or alicyclic group.

32. A composition as claimed in claim 31, wherein said macrocyclic polyester oligomer composition comprises less than 3% of macrocyclic polyester tetramers.

33. A process for modifying a melting temperature of a composition

comprising macrocyclic polyester oligomers, the process comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of the macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,

and

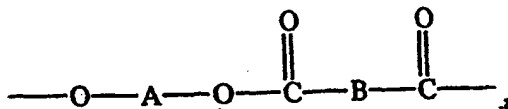
B is a divalent aromatic or alicyclic group; and

(b) performing fractional crystallization to reduce the weight percentage of at least one species of the macrocyclic polyester oligomers in the composition.

34. A process as claimed in claim 33, wherein the composition comprises at least two species of macrocyclic polyester oligomers having different degrees of polymerization.

35. A process for modifying a physical property of a composition comprising macrocyclic polyester oligomers, the process comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of the macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,

and

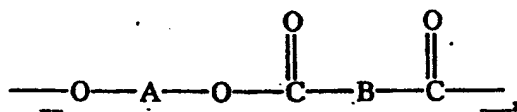
B is a divalent aromatic or alicyclic group; and

(b) performing anti-solvent precipitation to change the weight percentage of at least one species of the macrocyclic polyester oligomers in the composition.

36. A process as claimed in claim 35, wherein the composition comprises at least two species of macrocyclic polyester oligomers having different degrees of polymerization.

37. A process for modifying a melting temperature range of a composition comprising macrocyclic polyester oligomers, the process comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of the macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,

and

B is a divalent aromatic or alicyclic group; and

(b) changing the weight percentage of at least one species of the macrocyclic polyester oligomers in the composition.

38. A process as claimed in claim 37, wherein the at least one species of the macrocyclic polyester oligomers in step (b) comprises a macrocyclic polyester tetramer.

39. A process as claimed in claim 37 or 38, wherein the upper value of the melting temperature range is reduced.

40. A process as claimed in claim 39, wherein the upper value of the melting temperature range is reduced by at least 15°C.

41. A process as claimed in claim 39, wherein the upper value of the melting temperature range is reduced by up to about 70°C.

BEST AVAILABLE COPY

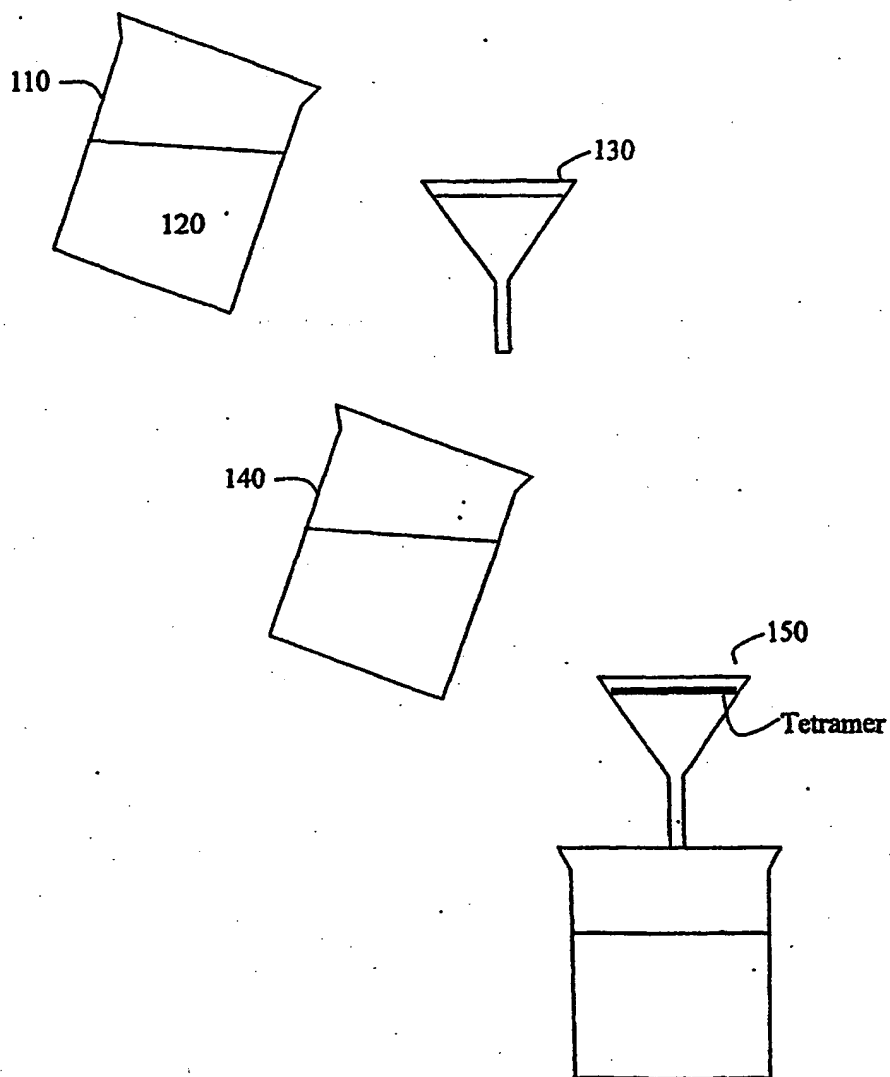


Fig. 1

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.